# CHAPTER LX

*CHROMIUM*

## § 1. The History and Occurrence of Chromium

In 1766, J. G. Lehmann [1] described *nova minera plumbi specie crystallina rubra* which he had obtained from Ekateribourg, Siberia, but for the next thirty years, the composition of the mineral was more or less conjectural. P. S. Pallas, indeed, said that it contained lead, sulphur, and arsenic. J. G. Wallerius called it *minera plumbi rubra ;* A. G. Werner. *rothes Bleierz ;* and L. C. H. Macquart, *plomb rouge de Sibérie—vide infra*, crocoite. J. J. Bindheim supposed the mineral to be a compound of molybdic acid, nickel, cobalt, iron, and copper. In 1794, L. N. Vauquelin in co-operation with L. C. H. Macquart, reported that it contained lead oxide, iron, alumina, and a large proportion—38 per cent.—of oxygen—*oxyde de plomb suroxygéne ;* but in 1797, L. N. Vauquelin, in his *Mémoire sur une nouvelle substance métallique, contenue dans le plomb rouge de Sibérie, et qu'on propose d'appeler chrome*, showed that the contained lead was united to a peculiar acid which was shown to be the oxide of a new metal to which he applied the name *chrom*—from χρῶμα, colour—*parce que ses combinaisons sont toutes plus ou moins colorées.* L. N. Vauquelin said :

> I observed that when the powdered mineral is boiled with a soln. of two parts of potassium carbonate, the lead combines with the carbonic acid, and the alkali, with the peculiar acid, to form a yellow soln. which furnishes a crystalline salt (potassium chromate) of the same colour. The mineral is decomposed by mineral acids, and when the soln. is evaporated it furnishes a lead salt of the mineral acid, and *l'acide du plomb rouge* (chromic acid) in long prisms the colour of the ruby. When the compound of *l'acide du plomb rouge* with potash is treated with mercury nitrate, it gives a red precipitate, the colour of cinnabar ; with lead nitrate, an orange-yellow precipitate ; with copper nitrate, a maroon-red, etc. *L'acide du plomb rouge*, free or in combination, dissolves in fused borax, microcosmic salt, or glass to which it communicates a beautiful emerald green colour.

L. N. Vauquelin isolated a pale-grey metal by heating a mixture of the chromic acid and carbon in a graphite crucible. About the same time as L. N. Vauquelin, M. H. Klaproth, in 1797, also demonstrated the presence of a new element in the red Siberian ore, but in a letter to *Crell's Annalen* he stated that L. N. Vauquelin had anticipated his discovery. M. H. Klaproth had dissolved the mineral in hydrochloric acid, and after crystallizing out the lead chloride, he saturated the liquid with sodium carbonate, and obtained the *Metallkalk*. He also noted the characteristic colour which it imparted to fused borax, and fused microcosmic salt. The results were confirmed by J. F. Gmelin, A. Mussin-Puschkin, S. M. Godon de St. Menin, and J. B. Richter. F. Brandenburg tried to show that the chromic acid of L. N. Vauquelin is really a compound of chromic oxide and one of the mineral acids, but K. F. W. Meissner, and J. W. Döbereiner proved this hypothesis to be untenable.

Chromium is widely diffused, but does not occur in the free state. F. W. Clarke [2] estimated that the igneous rocks of the earth's lithosphere contain 0·052 per cent. $Cr_2O_3$, 0·045 per cent. Cl, and 0·051 per cent. BaO. F. W. Clarke gave 0·37 per cent. Cr ; F. W. Clarke and H. S. Washington, 0·68 per cent. ; H. S. Washington

gave 0·20 per cent.; G. Berg, 0·033 per cent.; and J. H. L. Vogt, 0·01 per cent. W. Vernadsky gave 0·0033 for the percentage amount, and 0·01 for the atomic proportion. F. W. Clarke and H. S. Washington estimated that the earth's 10-mile crust, the hydrosphere and atm. contained 0·062 per cent. Cr; and the earth's 25-mile crust, the hydrosphere and atm., 0·65 per cent. of Cr. W. and J. Noddack and O. Berg gave for the absolute abundance of the elements in the earth: Cr, $3\times10^{-5}$; and Fe, $10^{-2}$; whilst A. von Antropoff obtained for the atomic percentages, 0·29 in stellar atmospheres; 0·021 in the earth's crust; 0·05 in the whole earth; and 0·29 in silicate meteorites. The subject was also discussed by V. M. Goldschmidt, G. Tamman, R. A. Sonder, P. Niggli, E. Herlinger, O. Hahn, J. Joly, and H. S. Washington. P. Pondal said that the proportion of chromium in basic rocks is greater than it is in acidic rocks where the proportion is very low or zero; he found 0·32 to 0·002 per cent. of $Cr_2O_3$ in 15 samples of Galician magmas.

Chromium occurs in minerals of extra-terrestrial origin. A. Laugier[3] found it in a meteorite from Vago. According to L. W. Gilbert, J. Lowitz had previously found chromium in a meteorite from Jigalowka, but the analysis was not published. Numerous analysis of other meteorites have been reported by E. Cohen, and others. J. N. Lockyer studied the spectra of meteorites. The general results show that chromium is a constant constituent of these meteorites. The amounts vary from 0·003 to 4·41 per cent. In most cases it is present as chromite; sometimes in the chondrite, olivine, pyroxene, pictotite, and *daubréeite*, $FeCr_2S_4$. H. A. Rowland,[4] T. Dunham and C. E. Moore, S. A. Mitchell, P. W. Merrill, H. Deslandres, G. Kirchhoff, J. N. Lockyer, and F. McClean, reported that the spectral lines of chromium appear in the solar or in stellar spectra. H. Deslandres also found chromium lines in the ultra-violet spectrum of the corona.

The principal mineral for the supply of chromium is *chromite*. It has a variety of names: *chrome ore*, *chrome-ironstone*, or *chrome iron ore*, $FeO.Cr_2O_3$, in which the iron and chromium are more or less replaced by magnesium and aluminium. Iron ore with up to about 3 per cent. of chromium is called *chromiferous iron ore*. The origin of the chromite deposits has been discussed by M. E. Glasser,[5] L. W. Fisher, E. Sampson, F. Ryba, C. S. Hitchin, J. S. Diller, P. A. Wagner, E. A. V. Zeally, J. H. L. Vogt, W. N. Benson, A. C. Gill, C. S. Ross, and J. T. Singewald. E. Sampson believed that although chromite may crystallize at a late stage as a magmatic mineral, a large proportion passes into a residual soln., or into a highly aq. soln. capable of considerable migration. The following analyses, Table I, were quoted by W. G. Rumbold:[6]

TABLE I.—ANALYSES OF CHROMITE ORES.

| Locality. | $Cr_2O_3$. | FeO. | MgO. | $Al_2O_3$. | $SiO_2$. |
|---|---|---|---|---|---|
| Baluchestan | 57·0 | 13·6 | 16·6 | 9·8 | 1·2 |
| Selukwe, Rhodesia | 46·5 | 15·7 | 11·7 | 15·5 | 8·0 |
| Canada | 46·0 | 22·5 | 4·9 | 8·9 | 7·7 |
| Urals, Russia | 55·8 | 21·6 | 13·9 | 3·3 | 5·4 |
| Orsova, Hungary | 39·0 | 16·1 | 17·2 | 17·5 | 8·0 |
| Asia Minor | 60·1 | 15·7 | 16·4 | 6·3 | 1·1 |
| California | 43·7 | 14·0 | 16·5 | 16·0 | 8·0 |
| North Carolina | 57·8 | 25·7 | 5·3 | 7·8 | 2·8 |
| New Caledonia | 54·5 | 17·7 | 8·0 | 11·1 | 3·1 |

The commercial value of the ore is based on the proportion of contained chromic oxide. The ore may be sold per ton; or per unit of contained chromic oxide over, say, a 50 per cent. standard. Prior to the Great War, Rhodesia and New Caledonia were the chief producing countries; during the years of the war, and with the lack of facilities for ocean freights, there were marked increases in output from

United States, India, and Canada. The geographical distribution of chrome ore is illustrated in a general way by the map, Fig. 1.

**Europe.**—In the **United Kingdom,**[7] deposits are associated with the serpentine near Loch Tay, and on the Island of Unst, Shetland. In **Austria,**[8] the ore has been worked in the Gulse Valley, and in Styria; in **Hungary,** at Orsova,[9] there are low grade ores at Ogradina, Dubova, Placishevitsa, Tsoritza, and Eibenthal; and in **Serbia,**[10] near Cacak. In **Germany,**[11] there is a large deposit of chromite on the south side of Mount Zobten, Lower Silesia; the exploitation of the chromite near Frankenstein, Lower Silesia, has not been a commercial success. In **Italy,**[12] at Ziona. **Greece**[13] has been a steady producer of chromite for many years; there are important deposits at Volo, and Pharsala; there are deposits in the provinces of Salonika, Lokris, and Boitio; and on the islands of Euboea, and Skyros. E. Nowack,[14] and D. A. Wray described the deposits in Macedonia and **Albania.** In **Turkey,**[15] there are deposits of chrome iron ore. In **Norway,**[16] there are deposits at Trondhjem, and Röraas; those in **Sweden** were discussed by F. R. Tegengren.[17] In **Portugal,**[18] there is a deposit near Braganca: and in **Spain,**[19] near Huelva. **Russia**[20] is rich in chromite ore, and was formerly a large producer. Chrome ore is found associated with the soapstones and serpentines of the Ural Mountains—*e.g.* on the banks of the Kamenka and Fopkaja. Masses of chromite occur at Orenburg. In **Jugoslavia** chrome

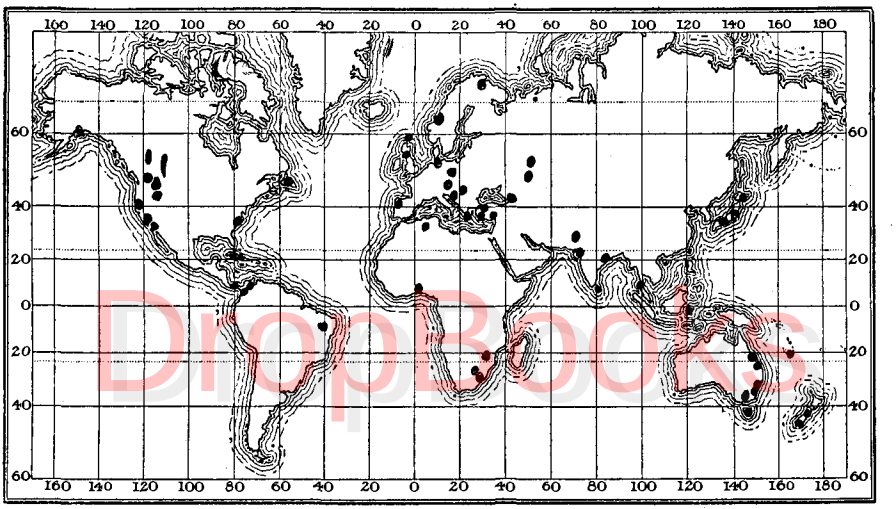


FIG. 1.—Geographical Distribution of Chrome Ores.

ore occurs at Ridjerstica in Serbia; and in the valleys of Dubostica, Tribia, and Krivaia in Bosnia.[21] Chromite also occurs at Raduscha, and the provinces of Kossovo and Monastir. P. Lepez,[22] E. Nowack, and D. A. Wray described the deposits of north-west **Macedonia.**

**Asia.**—In Northern **Borneo,** there are deposits on the Malliwalli Island, and chromite sands on the Marasinsing Beach. In the Islands of **Celebes,**[23] also, there are chromite sands. In **Ceylon,** alluvial chromite occurs in the Bambarabotuwa district. In **India,**[24] chromite occurs in the periodotite rocks near Salem, Madras, and also in the Andaman. There is a deposit near Khanogia, Pischin, and in the districts of Mysore, Hassan, and Shimoga of the State of Mysore. There are also deposits of chromite in Bihar and Orissa of the Singhbhum district near Retnagiri, Bombay Presidency; and in the Hindubagh district of Baluchistan. In **Asia Minor,**[25] deposits were discovered in 1848; and from about 1860 to 1903, that country supplied about half the world's output. There are several mines near Brusa. There are also deposits in Smyrna, Adana, Konia, and Anatolia. In the **Netherlands East Indies,** there is a deposit to the north of Malili, Celebes. In **Japan,**[26] there are deposits at Wakamatsu, Province of Hoki, and at Mukawa, Province of Iburi.

**Africa.**—In **Rhodesia,**[27] the deposits near Selukwe, Southern Rhodesia, have for some years yielded a larger output than any others. There are also deposits in Lomagundi, Victoria, and Makwiro. In **Natal,** chromite occurs at Tugela Rand, near Krantz Kop. In the **Transvaal,**[28] chromite occurs west of Pretoria; and in the districts of Lydenburg, and Rustenberg. In **Togoland,**[29] West Africa, there is a deposit between Lome and Atakpame. It also occurs in **Algeria.**

**America.**—In **Alaska,**[30] there are deposits of chromite on the Red Mountain, Kenai

peninsula. In **Canada,**[31] chromite occurs in the neighbourhood of Coleraive, Thetford and Black Lake in the Province of Quebec. The Mastadon claim, British Columbia,[32] produced about 800 tons of chromite in 1918. There are deposits at Port au Hay, at Benoit Brook, and near the Bay d'Est river, Newfoundland. Many deposits of chromite occur in the **United States.** It occurs in thirty-two counties of the State of California: [33] Alameda, Amador, Butte, Calaveras, Colusa, Del Norte, El Dorado, Fresno, Glenn, Humboldt, Lape, Mariposa, Mendocino, Monterey, Napa, Nevada, Placer, Plumas, San Benito, San Luis Obispo, Santa Barbara, Santa Clara, Shasta, Sierra, Suskiyow, Sonoma, Stanislaus, Tehama, Trinity, Tulare, and Tuolumine; near Big Timber, and Boulder River, in Montana; at Mine Hill, and near Big Ivey Creek,[34] North Carolina; at Golconda, Oregon; [35] in Maryland; [36] in Wyoming; and on the Pacific Coast.[37] There are also chromite deposits in **Nicaragua,** in the Jalapa County, **Guatemala;** and in several parts of **Cuba.**[38] In **Brazil,**[39] there are deposits north-west of Bahia; and in **Colombia,** at Antioquia.

**Australasia.**—In **New Caledonia,**[40] important deposits are located amongst the mountains in the southern part of the Island. In **Australia,** there are deposits between Keppel Bay and Marlborough, Queensland; [41] near Nundl, Pueka, and Mount Lighting, New South Wales; Gippsland, Victoria; and North Dundas, and Ironstone Hill, Tasmania: and a chromiferous iron ore occurs at North Coolgardie, West Australia. In **New Zealand,**[42] chromite deposits occur at Onatea, Croiselles Harbour; in the Dun Mountain; Moke Creek, Milford Sound, in Otago; and between D'Urville Island and the gorge of Wairva River.

In 1924, the price of chrome ore ranged from 9*s.* 6*d.* to 11*s.* per unit. The world's production of chromite ore in 1913 and 1916, expressed in long tons of 2240 lb. avoir., was respectively, India, 5676. and 20,159; New Caledonia, 62,351, and 72,924; South Rhodesia, 56,593, and 79,349; Canada, —, and 24,568; Australia, 677, and 451; Bosnia, 300, and —; Greece, 6240, and 972; Japan, 1289, and 8147; and the United States, 255, and 47,034. The World's productions in these years were respectively 133,381 and 262,353. For 1922, the results were:

| | | | |
|---|---|---|---|
| United Kingdom | 595 | Russia | 1,500 |
| South Rhodesia | 83,460 | Cuba | 1 |
| Union South Africa | 86 | Guatemala | — |
| Canada | 685 | United States | 420 |
| India | 22,777 | Brazil | — |
| Australia | 529 | Asia Minor | 2,500 |
| Greece | 9,768 | Japan | 3,696 |
| Jugoslavia | 16 | New Caledonia | 19,063 |
| Rumania | 30 | | |
| | | World | 145,000 |

The minerals containing chromates include natural lead chromate, **crocoite,** or **crocoisite,** $PbCrO_4$; **phoenicochroite,** or **melanochroite,** or **phoenicite,** $3PbO.2CrO_3$; **beresowite** or **beresovite,** $6PbO.3CrO_3.CO_2$; **vauquelinite,** and **laxmannite,** $2(Pb,Cu)CrO_4.(Pb,Cu)_3(PO_4)_2$; **tarapacaite,** $K_2CrO_4$, mixed with sodium and potassium salts; **jossaite** contains chromates of lead and zinc; **dietzeite,** an iodate and chromate of calcium. These are also **daubreeite,** $FeCr_2S_4$; **redingtonite,** a hydrated chromic sulphate; **chromite,** $FeO.Cr_2O_3$; **magnochromite,** $(Mg,Fe)O.Cr_2O_3$; and **chromitite,** $(Fe,Al)_2O_3.2Cr_2O_3$.

C. Porlezza and A. Donati [43] observed the presence of chromium in the volcanic tufa of Fiuggi; and A. Donati, in the products of the Stromboli eruption of 1916. There is a number of silicate minerals containing chromium; in some cases the chromium is regarded as an essential constituent; in others, as a tinctorial agent—R. Klemm. The chromosilicates have been previously discussed—**6.** 40, 865. There are the calcium chrome garnet, *uwarowite;* the hydrated chromium aluminium iron silicate, *wolchonskoite;* the bright green, clayey *chrome ochre—selwynite, milochite, alexandrolite, cosmochlore* or *cosmochromite;* the chrome-augite, *omphacite* or *omphazite;* the augitic *diaclasite;* the *chromediopside; chromdiallage;* the *chrome-epidote* of F. Zambonini [44] or the *tawmawite* of A. W. G. Blaeck; the chromic mica *fuchsite;* the chromic muscovite, *avalite;* the chromic chlorite *kämmererite*—and the variety *rhodochrome;* as well as *chromochlorite* or *rhodophyllite,* and *pennine;* the chromic clinochlor, *ripidolite,* and *kotschubeyite; serpentine;* and *chromotourmaline.*

P. Groth,[45] G. Rose, and A. Schrauf found chromium in *wulfenite*. The coloration of minerals by chromium was discussed by W. Hermann,[46] K. Schlossmacher, and A. Verneuil. The coloured alumina *smaragd*, *sapphire*, and *syenite* are chromiferous. Some spinels are chromiferous—*e.g.* *chromospinel*; and the so-called *picotite*, or *chromopicotite*, is a chromospinel; while *alexandrite* is a chromiferous beryl. K. A. Redlich[47] described a chromiferous *talc*; and K. Zimanyi. a chromiferous *aluminium phosphate*. Chromium occurs in the phosphate rocks of Idaho and Utah. B. Hasselberg reported traces of chromium in a specimen of *rutile* he examined spectroscopically; E. Harbich, in *amphibole*; and H. O'Daniel, in *pyroxene*; A. Jorissen found chromium in the *coal* of La Haye, and the flue-dust from this fuel had 0·04 per cent. of Cr. H. Weger reported chromium in a sample of *graphite*; F. Zambonini found chromium spectroscopically in vesbine of the crevices, etc., and in the Vesuvian lava of 1631. R. Hermann, A. Vogel, C. E. Claus, P. Collier, and G. C. Hoffmann observed chromium associated with native *platinum*; and J. E. Stead, with *iron*, and *steel*, and basic and other slags.

Compounds of chromium do not play any known part in the economy of animals or plants; and it has rarely been detected in animal or vegetable products. E. Demarçay[48] observed, spectroscopically, traces of chromium in the ash of Scotch fir, silver fir, vine, oak, poplar, and horn-beam; and L. Gouldin found it in the fruit of a rose.

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## § 2. The Extraction of Chromium as Chromic Oxide or Chromate

When the chromite is disseminated in disconnected patches, it is mined by open quarries generally in terraces or benches; and when large, well-defined deposits occur, as at Selukwe, Rhodesia, underground workings are practicable. Chromite is not so hard as quartz, but it is tougher, and does not break so easily. The mining is therefore assisted by blasting. Hand concentration by sorting may be used. Here the ore is separated from waste by means of a hammer; the larger pieces of ore may be broken into coarse lumps in a jaw crusher, and passed on to a revolving table or endless belt for hand-sorting. For concentrating by gravity machines, the ore is crushed moderately fine in a drop-stamping machine or in a ball mill, and then passed by water over a table concentrator whereby it is separated into (i) concentrate—consisting of chromite only; (ii) middling—containing much chromite; (iii) tailings—containing but little chromite and is sent to waste-dump; and (iv) slimes—often containing much chromite in a fine state of subdivision but not usually sufficient to deal with profitably. The middling is re-treated usually on another concentrating table. The tailings and slimes represent loss. The concentrate varies in quality, but it usually exceeds 50 per cent. chromite.[1]

Chromite can be converted into chromic oxide or chromate, by

1. *Dry processes.*—Here the powdered mineral is mixed with an alkali, and something to keep the mass open and porous while it is roasted by an oxidizing flame, say, in a reverberatory furnace, so as to form alkali chromate: $2(FeO.Cr_2O_3)+4Na_2CO_3+7O=Fe_2O_3+4Na_2CrO_4+4CO_2$. This is extracted with water and converted into dichromate by treatment with acid; the dichromate is then reduced to insoluble chromic oxide and a soluble alkali salt which is removed by lixiviation with water. The reaction was studied by A. J. Sofianopoulos, and H. A. Doerner. Technical details are indicated in the usual handbooks.[2]

If calcium chromate be treated with a soln. of potassium sulphate, the calcium chromate is converted into calcium sulphate, which is precipitated, and potassium chromate, which remains in soln. Instead of leaching the calcium chromate with a soln. of potassium sulphate, W. J. Chrystal showed that if ammonium sulphate is used, a soln. of ammonium chromate is produced, and J. J. Hood found that if the soln. of potassium salt be treated with sodium hydrosulphate, potassium sulphate crystallizes from the soln., while sodium dichromate remains in soln. According to F. M. and D. D. Spence and co-workers, if a mixture of ammonia and carbon dioxide be passed into the aq. extract of the calcium chromate, calcium carbonate is precipitated while ammonium and alkali chromate remain in soln. If the liquid be boiled, ammonia is given off, and sodium dichromate remains in soln. S. Pontius used water and carbon dioxide under press. for the leaching process. J. Brock and W. A. Rowell purified alkali chromite by treating the soln. with strontium hydroxide, and digesting the washed precipitate with a soln. of alkali sulphate or carbonate; W. J. A. Donald used calcium hydroxide or barium chloride as precipitant. A mixture of chromite with calcium carbonate and potassium carbonate was formerly much employed. Modifications of the process were described by W. J. A. Donald,[3] A. R. Lindblad, C. J. Head, S. G. Thomas, W. Gow, J. Stevenson and T. Carlile, L. I. Popoff, G. Bessa, P. Weise, P. N. Lukianoff, B. Bogitch, E. Baumgartner, W. Carpmael, Grasselli Chemical Co., N. F. Yushkevich, A. J. Sofianopoulos, R. W. Stimson, H. Specketer and G. Henschel, and C. S. Gorman. J. Booth, and S. G. Thomas heated the chromite to a high temp. before it was treated with the lime-alkali mixture. With the idea of lowering the temp. at which the chromate is formed, F. O. Ward recommended adding calcium fluoride to the mixture; and J. Massignon and E. Vatel added calcium

chloride. V. A. Jacquelain recommended calcining a mixture of calcium carbonate and chromite; extracting the calcium chromate with hot water; acidifying the soln. with sulphuric acid; and precipitating the iron by the addition of a little calcium carbonate. The soln. of calcium dichromate can be treated with alkali for the alkali salt. P. Römer used alkali carbonate without the calcium carbonate; the Chemische Fabrik Billwärder digested the chromite with sodium hydroxide in an iron vessel at 500°–600° through which was passed a current of air, an oxidizing agent was also added to the mixture. H. Moissan treated ferro-chromium with fused potassium hydroxide. The Chemische Fabrik Griesheim-Elektron used a modification of the process. G. Wachtel studied the effect of the lime. He said that with lime alone there is a 90 per cent. conversion of chromic oxide used and a 30 per cent. conversion with chromite; and that about 10 per cent. of the chromic oxide acquires the property of dissolving in acids. The yield with potassium carbonate alone is only half as large as when the potassium carbonate is mixed with an equal quantity of lime. Hence, the simultaneous action of the calcium and potassium carbonate on the ore gives better results than when either is used alone. N. F. Yushkevich observed that the formation of chromate with the chromite-lime-sodium carbonate mixture is slow at 700°; at 1160°, 95 per cent. of the chromium is oxidized in thirty minutes; and at 1260° decomposition sets in. L. I. Popoff found that the speed of oxidation of rich ores is quicker than with poor ores, and the percentage yield of chromate is greater. If the chromite contains 30 to 40 per cent. $Cr_2O_3$, lime to the extent of 80 per cent. of the weight of the ore should be added; 90 per cent. of lime for 40 to 50 per cent. ores; and 120 to 130 per cent. of lime for over 50 per cent. ores. These quantities of lime must be increased if the temp. of oxidation exceeds 1100°. The theoretical quantity of sodium carbonate was used. H. Pincass discussed this subject. P. Römer, and N. Walberg recommended using sodium carbonate in place of the more expensive potassium carbonate. Other alkali salts have been substituted for the carbonate; thus, S. Pontius, R. A. Tilghman, and H. M. Drummond and W. J. A. Donald used alkali sulphate; J. Swindells, sodium chloride; E. P. Potter and W. H. Higgins, sodium sulphate; E. Hene, alkali hydroxide; L. N. Vauquelin, J. B. Trommsdorff, and J. F. W. Nasse, potassium nitrate; and C. S. Gorman heated a mixture of chromite, sodium chloride, and calcium hydroxide in steam at 550°–850°. H. Schwarz found that by using alkali sulphate the potassium chromate can be leached directly from the mass. Instead of using calcium carbonate, C. S. Gorman used magnesium or barium carbonate; F. F. Wolf and L. I. Popoff, iron oxide; H. A. Seegall, barium carbonate; and the Deutsche Solvay-Werke, ferric oxide. P. Monnartz made the ore into briquettes with sand, limestone, and tar; these were fed into a small blast furnace using a blast of air enriched with oxygen. The products were a ferro-chromium alloy, and a slag with 9·4 per cent. chromic oxide. Modifications of the roasting process for chromates were employed by C. Häussermann, F. Filsinger, H. A. Seegall, and J. Uppmann for recovering chromium from chromiferous residues.

W. H. Dyson and L. Aitchison [4] heated chromite mixed with a carbonaceous material to 900° in a mixture of equal vols. of hydrogen chloride and chlorine until all the iron had volatilized; the residue was then heated to 1200° in the same gases to distil off the chromium. W. Crafts reduced the ore with charcoal at 1300° to 1350°, extracted the product with conc. sulphuric acid at 100°; and the chromium may be precipitated by adding calcium chloride to convert the sulphate to chloride and precipitating as hydroxide by limestone; or the chromium can be precipitated electrolytically from the sulphate soln. According to C. Müller and co-workers, chromite is first reduced in hydrogen or in a mixture of gases containing hydrogen and the product is heated above 200° with a slight deficiency of sulphuric acid in a closed vessel lined with hard lead containing preferably 3 per cent. of Sb.

Soln. of chromates can be reduced to chromic salt by hydrogen sulphide (L. N. Vauquelin),[5] sulphur dioxide (A. F. Duflos, and J. B. Trommsdorff), alkali

polysulphide (J. J. Berzelius), sulphur in a boiling soln. (G. F. C. Frick, J. L. Lassaigne, and H. Moser)—*vide infra*, chromic oxide.

2. *Wet processes.*—Chromates can be obtained from chromite or chromic oxide in the wet-way. The Chemische Fabrik Griesheim-Elektron [6] digested the powdered mineral with sulphuric acid of sp. gr. about 1·54 with an oxidizing agent like lead or manganese dioxide, potassium permanganate, etc. E. Müller and M. Soller used lead dioxide; E. Bohlig, potassium permanganate; E. Donath, manganese dioxide; P. Waage and H. Kämmerer, bromine; F. Storck and L. L. de Koninck, chloric acid; H. Dercum, G. Feyerabend, W. Stein, and M. Balanche, bleaching powder; and R. von Wagner used a mixture of sodium hydroxide and potassium ferricyanide. The chromium can also be extracted from chromite with acids, etc.

3. *Electrolytic processes.*—R. Lorenz [7] found that a soln. of potassium dichromate can be prepared by passing a current at 2 volts potential between an anode of ferrochrome (containing about equal quantities of chromium and iron) and a cathode of porous copper oxide, the two electrodes dipping in a soln. of potassium hydroxide contained in a beaker. Ferric oxide collects at the bottom of the beaker. The Chemische Fabrik Griesheim-Elektron obtained chromates by electrolytic oxidation with an anode of chromium, or of a chromium alloy—*e.g.* ferrochromium, an iron cathode, and a soln. of an alkali hydroxide separating the anode and cathode by a diaphragm. Sufficient alkali is added to the anode liquid to precipitate the metal alloyed with the chromium of the anode. Chromic acid and ferric sulphate can be separated by fractional crystallization. A modification of the process consists in dissolving the chromium or ferrochromium instead of using it directly as anode and then electrolyzing it, using an insoluble anode, such as lead. The cathode and anode compartments are separated by two diaphragms, and a hydroxide or a carbonate is added to the electrolyte contained in the compartment between the latter. J. Heibling used an alkali chloride or nitrite soln. as anolyte.

C. Häussermann [8] oxidized electrolytically a soln. of chromic hydroxide in soda-lye in the anode compartment, when the cathode liquid was a soln. of an indifferent salt; D. G. Fitzgerald used an acidic soln. of chromic oxide as anode liquor, and a soln. of a zinc salt about the cathode, and on electrolysis, chromate was formed at the anode and zinc was deposited on the cathode. K. Elbs said that a current efficiency of 70 per cent. can be obtained with freshly-ignited platinum anodes of low current density. F. Regelsberger had no success in the oxidation of chromium salts in acidic soln., even with the use of a diaphragm; but good results were obtained with alkaline soln., using lead anodes, with or without a diaphragm, with warm soln. M. de Kay Thompson studied the production of chromates by the electrolysis of sodium carbonate or hydroxide soln. with ferrochromium electrodes. E. Müller and M. Soller said that chrome alum dissolved in $N$-$H_2SO_4$ is not appreciably oxidized to chromic acid by the use of an anode of smooth platinum; but a trace of lead in the soln. is precipitated on the anode as lead dioxide, and this brings about oxidation; traces of chlorine also favour the oxidation. There is about one-third the oxidation with a platinized platinum anode as occurs with a lead dioxide anode. With a lead dioxide anode, the oxidation is almost quantitative in fairly conc. soln. of chrome alum, and a current density of about 0·005 amp. per sq. cm. The difference is not due to the higher potential of the lead dioxide anode, but rather depends on the lead dioxide acting catalytically as a carrier of oxygen. I. Stscherbakoff and O. Essin found that in the electrolytic production of dichromate from chromate a sudden rise in the conductivity of the electrolyte is observed when the composition corresponds to the polychromate, $Na_2Cr_4O_{12}$. In order to obtain the best yields of dichromate, electrolysis may be conducted either in normal chromate soln. at high current density or at lower current density in soln. of the above polychromate composition. According to F. Schmiedt, and A. R. y Miro, the oxidation is favoured by the presence of fluorine ions; and M. G. Levi and F. Ageno added that with normal soln. of chromium sulphate and $N$-$H_2SO_4$, on electrolysis with platinized platinum

electrodes in the presence of 0·498*N*-hydrofluoric acid, the yield of 78 per cent. chromic acid is comparable with that produced by lead dioxide electrodes. The Höchster Farbwerke said that in the electrochemical oxidation of a soln. of chrome alum to chromic acid, it is necessary for conc. sulphuric acid to be present, because, added F. Fichter and E. Brunner, the acid must be conc. enough to furnish sulphur tetroxide. F. Schmiedt found that the oxidation is favoured by the presence of Cy-ions (*e.g.* potassium cyanide or ferrocyanide), many oxidizing agents, compounds of phosphorus and boron, cerous nitrate, sodium molybdate or vanadate, and platinum tetrachloride. The Chemische Fabrik Buckau found that the reduction of chromate by cathodic hydrogen, in cells without diaphragms, is avoided by the use of a little acetic acid or an acetate. The electrolytic oxidation of soln. of chromium salts was also examined by M. le Blanc, F. Regelsberger, F. W. Skirrow, A. R. y Miro, L. Darmstädter, H. R. Carveth and B. E. Curry, and the Farbewerke Meister Lucius and Brüning, A. W. Burwell, I. Stscherbakoff, A. Lottermoser and K. Falk, E. Müller and E. Sauer, R. E. Pearson and E. N. Craig, M. J. Udy, and R. H. McKee and S. T. Leo.

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## § 3. The Preparation of Chromium

H. N. Warren[1] reduced chromic oxide by heating in a current of *hydrogen* in a tube of compressed lime by means of the oxyhydrogen flame. W. Rohn obtained chromium by reducing chromic oxide at 1500° in a rapid current of hydrogen from which every trace of oxygen and water-vapour had been removed. J. Schilling heated ammonium chromate to whiteness in hydrogen diluted with nitrogen and obtained chromium. M. Billy passed the vapour of the chloride mixed with hydrogen over a boat containing sodium supported on a layer of sodium chloride at 400° to 420°; the hydrogen forms a layer of hydride, and this reduces the chloride, $CrCl_3+3NaH=Cr+3NaCl+3H$. M. A. Hunter and A. Jones reduced the chloride by heating it with sodium in a heavy steel bomb. As previously indicated, L. N. Vauquelin first prepared chromium metal by heating a mixture of chromic oxide and *carbon* in a graphite crucible; and J. B. Richter, and H. Moser obtained it in a similar manner. H. St. C. Deville melted the chromic oxide with not quite sufficient carbon for complete reduction at a temp. of boiling platinum in a lime crucible. According to H. Moissan, chromic oxide is reduced in a few minutes when mixed with carbon and heated in the electric arc furnace. If a large excess of carbon is employed, chromium carbide is formed. If crude chromium in a crucible lined with chromic oxide, and covered with chromic oxide is heated in the arc-furnace, chromium may be obtained free from carbon. If crude chromium is heated with an excess of chromic oxide, the resulting metal is partially oxidized

or burnt. Chromium may be obtained with 1·5–1·9 per cent. of carbon by heating the crude metal mixed with lime in an electric furnace. The carbon forms calcium carbide. It is not possible to remove all the carbon by means of lime because, when the proportion of carbon has been reduced below a certain point, an inverse reaction occurs resulting in the formation of crystallized chromium calcium oxide. H. C. Greenwood found that the reduction of chromic oxide by carbon begins at 1180°–1195°, and the reduction is not quantitative. W. B. Hamilton and F. Reid used carbon. W. P. Evans's attempts to obtain chromium from chromyl fluoride, carbon and silica were unsatisfactory. V. and E. Rouff heated an intimate mixture of alkali chromate with silica and carbon to redness, and obtained alkali silicate and chromic oxide which, when intimately mixed with carbon and heated, furnishes chromium. A. Steinberg and A. Deutsch heated to 1000°–1400° a mixture of carbon and an alkaline earth chromate, and obtained chromium. H. Debray showed that if lead chromate be reduced by carbon at a red-heat, lead can be removed from the regulus by means of nitric acid—chromium remains. W. B. Balantine used calcium carbide. J. E. Loughlin heated chromic acid with a mixture of potassium cyanide and carbon. E. Viel obtained chromium from ferro-chromium or other alloys by heating in a high-temp. furnace a mixture of the alloy with an alkaline earth silicate, or with carbon and lime or alumina. E. Kunheim also heated a mixture of chromic sulphate and carbon in an electric arc-furnace, and obtained chromium. A. Binet du Jassonneix found that a mixture of *boron* and chromic oxide in a magnesia crucible heated in the electric arc-furnace furnishes chromium ; if a carbon crucible is employed, the chromium always contains carbon. If the chromium boride be heated with copper in an electric furnace, and the product digested with nitric acid, chromium remains. H. Goldschmidt, L. Franck, T. Fujibayashi, and T. Goldschmidt found that chromic oxide can be reduced by the thermite process in which a mixture of chromic oxide and *aluminium* in a crucible is ignited by a fuse. E. Vigouroux, and J. W. Richards said that chromium produced by the thermite process is free from carbon. E. Vigouroux observed that a fairly pure product is formed by heating in a crucible lined with magnesia, a mixture of chromic oxide and 10–20 per cent. chromic anhydride incorporated with the necessary quantity of aluminium powder. A vigorous reaction ensues, and it is over in about a minute. The slag separates readily from the metal. The product contains 0·36–0·40 per cent. of silicon, and 0·74–0·85 per cent. of aluminium and iron. J. Olie used 20 grms. of a mixture of 50 grms. of fused and powdered potassium dichromate and 18 grms. powdered aluminium, together with 10 grms. of a mixture of 450 grms. of calcined chromic oxide and 160 grms. of powdered aluminium. T. Fujibayashi used chromic oxide (100 parts), calcium chromate (10–15 parts), and 90 per cent. of the calculated weight of powdered aluminium. An 85 to 92 per cent. yield was obtained and the resulting chromium contained 3 to 5 per cent. of aluminium. M. Yonezu used a similar process. T. Goldschmidt, M. le Blanc, and G. Döllner used *magnesium*, or a carbide, in place of aluminium in the thermite process ; T. Goldschmidt, a mixture of calcium and silicon in place of aluminium ; and W. Prandtl and B. Bleyer used a mixture of calcium and aluminium instead of aluminium alone ; A. Burger passed the vapour of *calcium* over heated chromic oxide ; and heated the product with dil. nitric acid until the acid began to boil ; the product was first washed with water, then with alcohol, and finally dried at 100°. He also obtained chromium by heating a mixture of a mol of chromic oxide and 3 gram-atoms of calcium in a sealed tube. B. Neumann reduced chromic oxide with *silicon* in an electric furnace ; F. M. Becket used the silicothermic process ; S. Heuland reduced the oxide with *calcium silicide* ; R. Byman, *ferrosilicon* ; D. W. Berlin, an aluminium silicide ; R. Saxon, *calcium carbide* ; and L. Weiss and O. Aichel, *mischmetall*.

H. Aschermann heated a mixture of chromic and *antimonious oxide* in an electric furnace, and found that the resulting alloy loses all its antimony at a white-heat. S. Heuland melted the chromium ore in an electric furnace with a reducing agent

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sufficient to produce only a small amount of metal which will contain all the deleterious impurities in the ores, *e.g.*, phosphorus, carbon, or iron. The remainder of the metal is then reduced from the fused slag by addition of calcium silicide. The Metal Research Co. heated in a blast-furnace a mixture of chromic oxide, a sodium compound, and carbon so that the sodium first liberated reduces the chromic oxide to chromium. Processes for the smelting of chrome ores were described by T. R. Haglund, Aktiebolaget Ferrolegeringar, W. Bennett, W. E. S. Strong and co-workers.

F. Wöhler heated in a crucible a mixture of chromic chloride, and zinc along with a mixture of potassium and sodium chlorides; and treated the regulus with dil. nitric acid to remove the zinc. 30 grms. of chromic chloride yielded 6 to 7 grms. of chromium. The process was used by W. Prinz, E. Jäger and G. Krüss, and E. Zettnow; and M. Siewert added that the product is always contaminated with silicon derived from the crucible. F. Wöhler said that there is no advantage in using magnesium or cadmium in place of zinc; but E. Glatzel preferred magnesium. J. J. Berzelius reduced dry chromic chloride with potassium; H. St. C. Deville, sodium; E. Frémy, sodium vapour; K. Seubert and A. Schmidt, magnesium; and L. Hackspill, calcium. H. C. P. Weber heated between 700° to 1200° a mixture of chromic chloride and iron in order to produce metallic chromium and volatilize ferric chloride. If the iron is sufficiently finely divided, and a relatively low temp. is employed for reduction, chromium is obtained in a finely-divided form. If solid pieces of iron are used and the reaction takes place below the m.p. of the metals, a coating of chromium is formed on the pieces of iron. If an excess of iron is used and a sufficiently high temp. is employed, an alloy of chromium and iron is produced. Chlorides of chromium and nickel may be similarly reduced together to form alloys or mixtures with each other or with iron. Chromic oxide may be employed and converted into chloride with carbon and chlorine. The reduction process is advantageously carried out in vacuo or in an inert atm. such as nitrogen. W. P. Evans reduced the vapour of chromyl fluoride by sodium at 400°, and also by zinc near its b.p. Z. Roussin treated a feebly acidic soln. of a chromic salt with sodium amalgam, and heated the resulting chromium amalgam in hydrogen so as to volatilize the mercury. H. Moissan, J. Férée, and C. W. Vincent used a similar process. According to C. Goldschmidt, crystalline chromium is formed when a soln. of, say, chromic nitrate is kept for some days in a tin vessel.

In 1854, R. Bunsen[2] obtained chromium by the electrolysis of an aq. soln. of chromous chloride. He said:

> The density of the current—that is, the strength of the current divided by the surface of the electrode at which the electrolysis occurs—is most important, for, with increasing current density, the power of the current to overcome chemical affinity also increases. For instance, if a current of constant current strength be sent through a soln. of chromic chloride, it depends on the area of the resulting electrode whether hydrogen, chromic oxide, chromous oxide, or chromium is formed. The relative amounts of the constituents of the electrolyte through which the current passes are of no less importance. . . . The reduction to the metal occurs with boiling conc. soln. when the reducing surface receives a current of 0·067 amp. per sq. cm. . . . By using a soln. of chromous chloride, containing some chromic chloride, continuous sheets of chromium can be obtained. These are quite brittle, and the surface lying against the platinum electrode is perfectly white and of a metallic lustre. Chemically pure chromium can be obtained only in this way. It resembles iron very much in external appearance, but it is more permanent in damp air, and when heated burns to chromic oxide. Hydrochloric and sulphuric acids dissolve it slowly to chromous salts with the evolution of hydrogen; and it is scarcely attacked by nitric acid even when boiling. . . . If the current density be gradually lowered, a point is soon reached when in place of the metal, there is a copious formation of anhydrous chromous-chromic oxide. This oxide can be made only in this way, and it is purified by long boiling with aqua regia. It is a black crystalline powder, soluble in no acid, and burning in air like pyrophoric iron with a lively deflagration, to form green chromic oxide. Its composition varies between $Cr_4O_5$ and $Cr_5O_6$—*vide infra*, chromic chromate.

According to E. Müller and P. Ekwall, in the electrolysis of a soln. of chromic acid using a carbon cathode, a film of chromic chromate begins to form at a

potential, measured against a normal calomel electrode, of +0·8 volt, while evolution of hydrogen begins at about —1·2 volt. With a platinum electrode, hydrogen evolution begins at about 0·4 volt, while the separation of chromium, which is contaminated with oxide, occurs at about —1·2 volt, and is preceded by the formation of the insoluble, colloidal chromic chromate film, which is first observed microscopically at —0·7 volt, and is pressed cataphoretically to the cathode. The gel is purified by dialysis, and is found to migrate to the cathode, where it is coagulated. The compound is soluble in acids and bases, and its composition corresponds to the formula $Cr_2(OH)_4CrO_4$. When present as a film, the molecules are oriented and form a diaphragm, which is impervious to $CrO_4''$ or $HCrO'_4$-ions, but allows $H^{\cdot}$-ions to pass. Reaction accordingly ceases until the hydrogen separation potential is exceeded when the film is broken and the reaction proceeds in accordance with the equation : $Cr_2(OH)_4CrO_4+2H_2CrO_4=2Cr'''+3CrO_4''+4H_2O$. Deposition of chromium then occurs, and the chromic chromate film is again formed. The deposition of successive layers of this film according to the magnitude of the applied potential is shown under the microscope by differences in colour. The presence of sulphuric acid in the electrolyte modifies the film formation and increases the intervals of exposure of the electrode, whereby greater accession of chromium ions results, while contamination of the deposited metal with oxide is suppressed. M. L. V. Gayler used a one per cent. sulphuric acid soln. of chromic acid. E. Müller and J. Stscherbakoff found that in spite of its strong oxidizing action, pure chromic acid is not electrolytically reducible in aq. soln., but it becomes so on addition of $SO''_4$-ions. They showed that the cathode becomes coated with an invisible, non-conducting, fine-grained layer, which prevents the reduction of chromic acid. This layer becomes charged in presence of $SO''_4$, but this occurs only after a certain cathode potential has been attained. It is hence concluded that charging by the $SO''_4$-ions necessitates the electrostatic attraction of these ions by the layer of colloid. S. Takegami also studied the deposit of colloidal chromic oxide.

R. Bunsen suggested that it would be worth trying to find if allotropic forms of chromium could be produced by electrolyzing green and blue chromic salt soln. Subsequent work, however—by W. R. Whitney, etc.—has shown the hypothesis to be untenable. S. O. Cowper-Coles obtained a bright deposit of chromium from a soln. of 25 parts of chromic chloride in 75 parts of water at 88°, with a current of 0·04–0·05 amp. per sq. cm. With a cold soln., gas is evolved at both electrodes, but no metallic deposit is obtained until an excess of hydrochloric acid is added. J. Férée found that a steel-grey deposit of chromium on a platinum cathode is formed with a soln. of chromic chloride acidified with hydrochloric acid ; and a silver-white deposit from a soln. containing potassium and chromic chlorides in the proportion of 1 : 3, and a current density of 0·15 amp. per sq. cm., and 8 volts. J. Voisin added that when the deposit is over 3 or 4 mm. thick, it is liable to peel off. The Wolfram-Lampen A. G. obtained chromium by the electrolysis of soln. of chromic chloride in acetone ; J. Roudnick, and G. Neuendorff and F. Sauerwald, by the electrolysis of the fused silicate.

S. O. Cowper-Coles found that a soln. of 100 parts of chrome-alum in 100 parts of water with 12 parts of barium sulphate does not yield a deposit of chromium metal on electrolysis. E. Placet found that when a soln. of chrome-alum and an alkali sulphate acidified with sulphuric acid, is electrolyzed, chromium is deposited at the cathode as a hard, bluish-white, lustrous metal, which, under certain conditions, crystallizes in groups resembling the branching of firs. Other metals and alloys—bronze, copper, iron, brass, etc.—may be plated with chromium, and a surface can be obtained to resemble oxidized silver. E. Placet and J. Bonnet have a number of patents on this subject.

Various baths have been recommended and the subject of chromium plating has been discussed by M. Alkan, J. D. Alley, C. M. Alter and F. C. Mathers, R. Appel, P. Askenasy and A. Révai, E. M. Baker and E. E. Pettibone, E. M. Baker and A. M. Rente, M. Ballay,

J. Bauer, F. M. Becket, R. Bilfinger, W. Birett, J. Blasberg, W. Blum, J. J. Bloomfield and W. Blum, G. le Bris, A. Champion, A. Butziger, Chemical Treatment Co., Chromium Corporation of America, A. J. Coignard, J. Cournot, W. Crafts, J. W. Cuthbertson, G. J. Delatre, S. Dreyfus, W. S. Eaton, C. H. Eldridge, P. W. Ellwanger, G. M. Enos, D. T. Ewing and A. K. Malloy, H. L. Farber and W. Blum, S. Field, C. G. Fink, C. G. Fink and C. H. Eldridge, J. H. Frydlender, G. P. Fuller, G. Fuseya and co-workers, G. E. Gardam, R. Grah, A. K. Graham, L. E. and L. F. Grant, F. Grove-Palmer, G. Grube, C. A. Guidini, O. Günther, O. Hahn, C. Hambuechen, J. Harden and H. T. Tillquist, H. E. Haring, H. E. Haring and W. P. Barrows, J. Hausen, E. V. Hayes-Gratze, J. M. Hosdowich, M. Hosenfeld, H. W. Howes, W. E. Hughes, T. W. S. Hutchins, V. P. Ilinsky and co-workers, R. Justh, E. Kalmann, Y. Kato and co-workers, D. B. Keyes and S. Swann, P. M. Killeffer, V. Kohlschütter and A. Good, E. Krause, F. Krupp, E. Kruppa, S. Kyropoulos, H. Lange, F. Lauterbach, E. Liebreich and co-workers, H. Leiser, P. Leistritz and F. Burghauser, B. F. Lewis, C. L. Long and co-workers, F. Longauer, H. S. Lukens, O. Macchia, J. F. K. McCullough and B. W. Gilchrist, D. J. MacNaughton and co-workers, B. Mendelsohn, Metal and Thermite Corporation, Metropolitan-Vickers Electrical Co., E. Müller, E. Müller and co-workers, M. Nagano and A. Adachi, National Electrolytic Co., W. Obst, Olausson and Co., E. A. Ollard, K. Oyabu, A. H. Packer, A. V. Pamfiloff and G. F. Filipuicheff, L. C. Pan, J. C. Patten, W. Pfanhauser, W. M. Phillips, W. M. Phillips and M. F. Macaulay, W. M. Phillips and P. W. C. Strausser, H. C. Pierce, H. C. Pierce and C. H. Humphries, R. J. Piersol, W. L. Pinner, W. L. Pinner and E. M. Baker, F. R. Porter, H. E. Potts, C. H. Procter, E. Richards, J. G. Roberts, J. Roudnick. G. F. Sager, F. Salzer, G. J. Sargent, V. Schischkin and H. Gernet, H. Schmidt, R. Schneidewind and co-workers, K. W. Schwartz, A. Siemens, E. W. M. von Siemens and J. G. Halske, J. Sigrist and co-workers, O. J. Sizelove, J. Stscherbakoff and O. Essin, W. Steinhorst, L. E. Stout and J. Carol, F. Studinges, H. E. Sunberg, V. Szidon, O. P. Watts, L. Weisberg and W. F. Greenwald, S. Wernick, H. Wolff, M. Wommer, L. Wright, F. W. Würker, and S. Yentsch.

J. F. L. Möller and E. A. G. Street obtained chromium by the electrolysis of an aq. soln. of chrome-alum and sodium sulphate at 90° with a current density of 0·4 amp. per sq. cm. R. Stahn electrolyzed soln. of chromous salts. J. Voisin also obtained no deposit of chromium with a violet soln. of chrome-alum mixed with potassium hydrosulphate, using a current density of 0·02 to 0·20 amp. per sq. cm. and 4 to 12 volts, and similarly with neutral and alkaline soln.; with a green soln. of chrome-alum and 0·18 amp. per sq. cm. a small, grey deposit of a substance soluble in hydrochloric acid was obtained. According to M. le Blanc, chromium deposits cannot be obtained in the manner described. Among other processes, the following can be used:

A sat. soln. of chromic sulphate at the temp. of the room, was used and 100 c.c. dil. to 600 c.c. with water and then sodium chloride added to saturation. A platinum foil was used as cathode. With 40 sq. cm. active cathode surface, using a current density of 0·2 amp. per sq. cm., there was obtained a quite small, black precipitate which from its behaviour appeared to be chromium. With a current density of 0·3 amp. per sq. cm. no precipitate was obtained. A precipitate did not appear when the above bath was sat. with sodium sulphate instead of sodium chloride and electrolyzed at 30° and 80° with a current of 0·2 and 0·3 amp. per sq. cm.

F. Adcock found that chromium of a high degree of purity can be obtained by the electrolysis of an aq. soln. containing 30 per cent. of purified chromic acid, and one per cent. sulphuric acid using tin or steel cathodes. In one with a steel cathode rotating 30 revs. per minute, the temp. of the bath was 20°, the voltage 5·2, and the amperage 140. The current densities at the cathode and anode were 28 amp. and 7·2 amp. per sq. dm., and the yield of chromium in 30 hrs. was 500 grms., with a current consumption of 8·3 ampère-hrs. per gram. All the samples as deposited contained hydrogen and oxygen, the former being liberated during remelting in vacuo. The cathode chromium is in a form which leaves no residue on dissolution in acid, and is converted, when heated in vacuo, into insoluble chromic oxide. This can be removed, however, by heating the solid metal in purified and dried hydrogen to 1500°–1600°. After these treatments, spectroscopic examination failed to reveal any impurities. T. Murakami studied the action of chemical reagents on the deposits.

B. Neumann and G. Glaser examined the influence of current strength, current density, conc., and temp. with different soln. of chromic salts. The diaphragm

cells contained the chromium salt soln. in the cathode compartment, and a mineral acid or salt soln. in the anode chamber. The cathode was ordinary carbon, but the deposited chromium was found to adhere also to cathodes of borax, lead, or platinum; the anode, according to the soln. employed, was lead, platinum, or carbon. If the cathode soln. is not well circulated, it becomes impoverished at the cathode, and with high current densities only the chromosic oxide is deposited. Using a chromic chloride soln. with 100 grms. of Cr per litre, at the temp. of the room, and with current densities less than 0·072 amp. per sq. cm., the deposit consisted of metal mixed with more or less of the chromosic oxide; and with current densities 0·091 to 0·182 amp. per sq. cm., metal alone was deposited with a 38·4 to 38·6 per cent. ampère output. The deposit is good up to about 50°, but beyond that the chromium deposits as a black powder. With a constant current density and with soln. containing 184 grms. of Cr per litre and over, the deposit was a metallic powder; with soln. containing respectively 158, 135, and 105 grms. of Cr per litre, the percentage ampère outputs of pure metal were respectively 50·6, 49·0, and 38·4; with soln. containing 179 grms. of Cr per litre, at first metal and the chromosic oxide were deposited; and with 53 or less grms. of Cr per litre, chromosic oxide and hydrogen were formed. Sulphate and acetate soln. give similar results except the numerical values differed from those just indicated. The acetate soln. gave imperfect precipitates, and poor yields; the best yield—84·6 per cent.—with sulphate soln. occurred with soln. containing 65–85 grms. of Cr per litre, and a current density of 0·13 to 0·20 amp. per sq. cm. B. Neumann, and G. Glaser concluded that the influence of temp. is of slight importance, but H. R. Carveth and W. R. Mott found that with chloride soln. a rise of temp. caused a marked decrease in efficiency. The electrodeposition of chromium was also investigated by J. Sigrist and co-workers, and E. F. Smith. S. Kyropoulos found that chromium is deposited more freely in isolated spots on the crystal faces of tempered aluminium. A higher current density favours deposition on the crystal faces. Deposition on the crystal faces is favoured by conditions such that the production of hydrogen at the cathode is possible. Resistance to copper deposition is most clearly shown by passive chromium, deposition occurring only on isolated spots of non-passive chromium; with hydrogen evolution at the cathode, deposition occurs on the crystal faces of the chromium.

According to H. R. Carveth and W. R. Mott, in the electrolysis of a soln. of chromic chloride containing 100 grms. of Cr per litre, at 21°, and a current density of 0·5 amp. per sq. cm., the efficiency slowly increased until a constant value of about 30 per cent. was attained. This phenomena was attributed to the formation of chromous chloride which is assumed to be necessary for efficient electrolysis—raising the temp. acts deleteriously by increasing the rate of oxidation of chromous chloride. The bubbling of air through the soln. diminished the efficiency. Variations in the nature of the anode liquid caused considerable alterations in the efficiency; high values were obtained with an anolyte of ammonium sulphate, due, it is supposed, to diffusion into the cathode chamber. O. Dony-Hénault added that the formation of chromous chloride is not the only condition required for the deposition of chromium from a soln. of chromic salt. During the electrolysis of a soln. of chrome-alum, the green soln. becomes violet, and after a time deposits violet crystals of the alum. Chromium was deposited from the violet but not from the green soln.

According to J. Voisin, the electrolysis of a soln. of purified chromic acid gives 2 vols. of hydrogen and one vol. of oxygen as in the analogous case of sulphuric acid. The electrolysis of a soln. of ordinary chromic acid—260 grms. per litre—with a current density of 0·40 amp. per sq. cm. gives 0·250 grm. of white, adherent chromium per hour. Chromium anodes are preferable. The deposit is improved when 5–6 grms. of boric acid per litre are present. A sat. soln. of chromic hydroxide in hydrofluoric acid, and a current density of 0·2 to 0·20 amp. per sq. cm. and 12 volts gives no metal, but a green deposit of $Cr_2O_3.9H_2O$ appears on the cathode.

H. R. Carveth and B. E. Curry found that chromium begins to be deposited instantly from a soln. of impure chromic acid at 18° with a current density of about 0·80 amp. per sq. cm. The deposition is not so readily obtained with soln. of purified chromic acid which has a decomposition voltage of 2·31 volts. In all cases, the liquid was coloured brown, and chromic salts were produced; the brown precipitate formed at the cathode is probably $Cr(CrO_4)$. It is assumed that sexivalent chromium cations are present in the soln. of chromic acid, and that the increased deposition which occurs when sulphuric acid is present, is due to an increase in the conc. of the sexivalent Cr-cations by a reaction of chromic acid with the sulphuric acid. F. Salzer found that the deposits of chromium are produced with a bath of approximately equal proportions of chromic acid and chromic oxide; or preferably with an excess of chromic acid. The quantities should be kept nearly constant during the electrolysis, and the temp. maintained constant by cooling the bath. Anodes, capable of oxidizing the chromium oxide to chromic acid during the passage of the current, may be employed, in order to maintain a constant composition in the bath by compensating for the chromic acid reduced at the cathode, or insoluble anodes, such as lead or platinum, may be used to maintain a constant composition, these being in part freely suspended in the bath, and in part separated from the cathode chamber by convenient diaphragms. The subject was investigated by E. Liebreich, E. Müller, E. Müller and P. Ekwall, and G. Grube and G. Breitinger.

A. Krupp prepared chromium of a high degree of purity by electrolyzing a fused chromium halide using impure chromium as anode. The electrodeposition of chromium has been investigated by R. Appel,[3] C. L. Long and co-workers, G. Neuendorff and F. Sauerwald, and F. Andersen. R. Taft and H. Barham studied the electrodeposition of chromium from soln. of its salts in liquid ammonia.

H. Moissan, and J. Férée prepared *pyrophoric* chromium by distilling the amalgam in vacuo at 300°, but if heated more strongly, it loses its pyrophoric activity. H. Küzel obtained **colloidal chromium** by bringing the element to a fine state of subdivision by grinding, or by cathodic disintegration. It was then converted into the colloidal state by repeated alternate treatments for long periods with dil. acid soln. and dil. alkaline or neutral soln., under the influence of moderate heat and violent agitation. After each treatment the material was washed with distilled water or other solvent until completely free from the reagent employed. T. Svedberg also prepared **chromium hydrosol** by his process of cathodic disintegration; and with isobutyl alcohol as the liquid menstruum, **chromium *iso*butylalcosol** was obtained. G. Bredig did not obtain much success with splutterings from an electric arc under water.

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## § 4. The Physical Properties of Chromium

The specimens of chromium prepared by the early investigators were more or less impure, and in some cases the impurity affected the physical properties to an appreciable extent. The metal prepared by the carbon reduction process is contaminated with carbon or carbides; and that prepared by aluminium reduction is contaminated with aluminium and silicon. Chromium prepared by heating the amalgam to about 300° is a black pyrophoric grey powder—*vide supra*. R. Bunsen [1] found that the electrolytically deposited metal to be steel-grey or silver-white. H. Moser described chromium as a steel-grey mass composed of four-sided prisms; and J. F. Gmelin obtained a metal with a dull-grey fracture and interspersed with tin-white crystals. E. Glatzel obtained chromium as a micro-crystalline, grey powder; F. Wöhler obtained it in the form of what he called grey rhombohedra; E. Jäger and G. Krüss, tin-white rhombohedra; P. A. Bolley, tetragonal pyramids; E. Frémy, and E. Zettnow, in cubic crystals; and W. Prinz said that when prepared by F. Wöhler's process, the minute cubes with pyramidal faces furnish hexagonal and octahedral contours when examined by transmitted light; and he added that the supposed rhombohedra are probably deformed octahedra. W. C. Phebus and F. C. Blake found that the **X-radiogram** agrees with a body-centred cubic lattice, with side $a=2{\cdot}875$ A. A. W. Hull gave for the side of the elementary cube of the body-centred cubic lattice, 2·895 A.; for the distance between the nearest atoms, 2·508 A.; and for the density, 7·07; R. A. Patterson, and F. Sillers gave $a=2{\cdot}872$ A.; E. C. Bain, $a=2{\cdot}899$ A.; and W. C. Phebus and F. C. Blake, $a=2{\cdot}875$ A. for the body-centred cubic lattice. W. P. Davey and T. A. Wilson, E. Schmid, R. Blix, W. Hume-Rothery, and G. F. Hüttig and F. Brodkorb made observations on this subject. H. L. Cox and I. Backhurst observed no marked effect on the X-radiograms for stresses below the elastic limit. A. J. Bradley and E. F. Ollard said that the electro-deposited chromium may exhibit **allotropy,** for it may show the hexagonal structure as well as the body-centred cubic structure. C. S. Smith observed only the latter form. The subject was discussed by F. Adcock; and H. Shoji studied the mechanism of the change of the space-lattice in passing from one allotropic form to another. A. W. Hull added that iron and chromium have a similar arrangement of atoms in the space-lattice, and this shows that ferro-magnetism does not depend on a particular arrangement of the atoms. On the other hand, A. J. Bradley and E. F. Ollard said that the X-radiogram agrees with the assumption that chromium is a mixture of two allotropes. In the predominating form, the atoms are arranged in two hexagonal lattices giving an almost hexagonal close-packed structure, the axial ratio $a:c$ being 1·625 instead of 1·633, and the distance between neighbouring atomic centres 2·714 A. and 2·70 A.

J. B. Richter gave 5·9 for the **specific gravity** of chromium; F. Wöhler, 6·81 at 25°; J. E. Loughlin, 6·2; C. F. Rammelsberg, 6·522; R. Bunsen, 6·7; E. Glatzel, 6·7179–6·737 at 16° for the crystalline powder; A. Gotta, 7·0367 to 7·0747 at 25°; H. Moissan, 6·92 at 20° for the metal previously fused in an electric furnace; A. Binet du Jassonneix, 7·1 at 17° for metal derived from the boride; and T. Döring 7·085 for 98 per cent. chromium prepared by the alumina-thermite process. K. Honda gave 6·8 for a sample with over 20 per cent. of iron. K. Ruf gave 7·014

at 20° for the pure metal, and 7·011 for electrolytic chromium. G. F. Hüttig and F. Brodkorb found that electrolytic chromium free from occluded gas had a sp. gr. of 7·138 at 25°/4°, and 7·156 at −50°/4°; hence the **atomic volume** is 7·286 at 25° and 7·268 at −50°. H. Schröder discussed the volume relations of the sulphates, selenates, and chromates; E. Donath and J. Mayrhofer, the at. vol.; and I. Traube, the at. soln. vol. E. M. Baker and A. M. Rente, and D. J. Macnaughtan discussed the porosity of electro-deposited chromium. M. L. Huggins calculated for the **atomic radius,** 1·44 A.; W. F. de Jong and H. W. V. Willems, 1·40 A. to 1·42 A.; and W. L. Bragg, 1·40 A. H. G. Grimm, V. M. Goldschmidt, L. Pauling, E. T. Wherry, J. C. Slater, and A. M. Berkenheim discussed this subject, from which it follows that for sexivalent chromium atoms, the effective at. radius is 0·52 to 0·65 A., and for typical atoms, 1·17 to 1·54 A. P. Vinassa studied the mol. number.

K. W. Schwartz said that the bluish-white metal is exceedingly hard and can be drilled only with difficulty. J. B. Dumas found that the chromium he prepared scratched glass of hardness 5·6 on Mohs' scale. H. St. C. Deville said that its **hardness** is equal to that of corundum; while H. Moissan said that it scratches glass only with difficulty; it can be polished readily and then shows a good reflecting surface. J. R. Rydberg gave 9 for its degree of hardness (diamond 10). According to F. Adcock, the great hardness of electrolytically-deposited chromium, 650 on Brinell's scale, is apparently caused by the occluded hydrogen, the crystalline form, and possibly the oxygen. It is not possessed by the metal of a high degree of purity melted or annealed at high temp. in vacuo or an atm. of hydrogen, the hardness being then as low as 70 on Brinell's scale. L. E. and L. F. Grant obtained the hardest deposits of chromium from a soln. of 209 grms. of chromic acid, 23 grms. of chromic oxide, and 6·4 grms. of chromic sulphate per litre using a current density of 33·3 amps. per sq. dm., at 45°. D. J. Macnaughtan and A. W. Hothersall gave 500 to 900 for Brinell's hardness of electro-deposited chromium; and D. J. Macnaughtan studied the porosity of the deposits. The subject was discussed by R. J. Piersol. W. Treitschke and G. Tammann found that the **viscosity** of chromium is very great when in the vicinity of the m.p. T. W. Richards found the **compressibility** of chromium, *i.e.* the mean change of vol. per megabar, between 100 and 600 megabars, to be $0{\cdot}7\times10^{-6}$ for 99 per cent. chromium. P. W. Bridgman found for the vol. compressibility from measurements of the linear compressibility, at 30°, $\delta v/v_0=-5{\cdot}187\times10^{-7}p+2{\cdot}19\times10^{-12}p^2$; and at 75°, $\delta v/v_0=-5{\cdot}310\times10^{-7}p+2{\cdot}19\times10^{-12}p^2$. These values are lower than the result given by T. W. Richards. W. Widder gave for the modulus of elasticity, $E=E_{20}\{1-0{\cdot}006536(\theta-20)\}$; M. Grube, C. J. Smithells and S. V. Williams, J. Laissus, W. van Drunen, and F. C. Kelley studied the **diffusion** of chromium with iron and nickel.

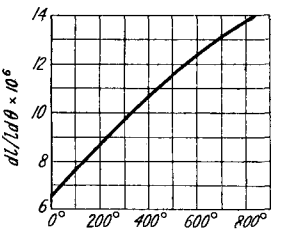

FIG. 2.—The Effect of Temperature on the Coefficient of Expansion.

J. Disch[2] found the coeff. of **thermal expansion**—linear—to be $0{\cdot}0_5731$ between −78° and 0°; and $0{\cdot}0_584$ between 0° and 100°. P. Chevenard found that the expansion curve is exactly reversible between 0° and 100° and shows no singular point. The true coeff. of expansion, 0·0000068 at 0°, increases rapidly with temp. and shows a slight concavity towards the increasing temp., Fig. 2. G. F. Hüttig and F. Brodkorb gave $1{\cdot}2\times10^{-5}$ for the coeff. of expansion between −50° and 25°. W. Widder gave $0{\cdot}0_5824$ at 20°. J. Disch gave for the linear expansion in mm. per metre:

| | −78° | 0° | 100° | 200° | 300° | 400° | 500° |
|---|---|---|---|---|---|---|---|
| Expansion . | −0·57 | 0·00 | 0·84 | 0·75 | 2·72 | 3·76 | 4·86 mm. |

E. Jäger and G. Krüss gave for the **specific heat** 0·12162 between 0° and 98·24°; H. Mache, 0·1208 between 0° and 100°; H. Schimpff 0·1044 at 0°; R. Lämmel

gave 0·0898 at −100°; 0·1039 at 0°, and 0·1872 at 600°. T. W. Richards and F. G. Jackson, 0·0794 between −188° and 20°; and P. Schübel gave for the true sp. ht., $c_p$, and the **atomic heat**, $C_p$:

| | 50° | 100° | 200° | 300° | 400° | 500° | 600° |
|---|---|---|---|---|---|---|---|
| $c_p$ | 0·1080 | 0·1160 | 0·1200 | 0·1211 | 0·1250 | 0·1340 | 0·1500 |
| $C_p$ | 0·63 | 6·05 | 6·25 | 6·30 | 6·50 | 6·99 | 7·81 |

S. Umino gave:

| | 100° | 300° | 500° | 700° | 900° | 1100° | 1300° | 1500° | 1640° |
|---|---|---|---|---|---|---|---|---|---|
| Sp. ht. | 0·118 | 0·123 | 0·131 | 0·144 | 0·158 | 0·177 | 0·200 | 0·225 | 0·187 |

F. Wüst, A. Meuthen and R. Durrer, and G. Tammann and A. Rohmann also made observations on the sp. ht. F. Michand, J. Maydel, and E. van Aubel discussed the at. ht. relations; and E. D. Eastman and co-workers, the thermal energy of the electrons in chromium, and computed $C_p - C_v = 0·037$ Cal. per degree per mol. P. Nordmeyer and A. L. Bernoulli gave 0·1039 for the sp. ht. at 0°; 0·1121 at 100°; 0·1236 at 300°; 0·1503 at 500°; and 0·0860 between −185° and 20°. J. Dewar gave 0·0142 between −253° and 196° with the at. ht. 4·14. F. Simon and M. Ruhemann gave $C_p = 1·249$ and $C_v = 1·247$ at 71·29° K.; and $C_p = 1·56$ and $C_v = 1·56$ at 79·50° K. R. Lämmel represented his results by $c_p = 0·103944 + 0·0_3 10591\theta - 0·0_6 29694\theta^2 + 0·0_9 54088\theta^3$; and F. W. Adler observed:

| | 0° | 100° | 200° | 300° | 400° | 500° | 600° |
|---|---|---|---|---|---|---|---|
| $c_p$ | 0·10394 | 1·11211 | 0·11758 | 0·12360 | 0·13343 | 0·15030 | 0·18710 |
| $C_p$ | 5·40 | 5·83 | 6·11 | 6·43 | 6·94 | 7·82 | 9·73 |

H. St. C. Deville[3] found that chromium melts at a higher temp. than is the case with manganese or platinum; and H. Moissan also stated that the **melting point** of chromium is much higher than that of platinum; for it cannot be fused by the oxyhydrogen blowpipe. E. Glatzel, however, fused it by the oxy-hydrogen flame. S. O. Cowper-Cowles gave 2000° for the m.p.; but this is too high. E. A. Lewis found that the metal made by the aluminium-thermite process melted at 1515° ± 5°. G. K. Burgess gave for 99 per cent. chromium, 1489°; E. Tiede and E. Birnbräuer, 1420°; E. Newbery and J. N. Pring, 1615° ± 15°; W. Treitschke and G. Tammann, 1513°; S. Umino, 1600° (95·39 per cent. Cr); R. S. Williams, and G. Voss, 1553°; K. Lewkonja, 1547°; J. Johnston, 1510°; G. Hindrichs, 1550°; and R. Vogel and E. Trilling give 1575°. K. Honda gave 1515° for a sample with about 20 per cent. of iron. W. Guertler and M. Pirini, W. R. Mott, and G. K. Burgess and R. G. Waltenberg gave for the best representative value 1520°; but L. I. Dana and P. D. Foote gave 1615°. A. von Vogesack said that the m.p. of chromium is over 1700°, and that the lower values are due to the presence of carbon obtained from the carbon monoxide in the atmosphere in which the metal is melted; whilst with C. J. Smithells and S. V. Williams, 1920° was thought to be a low value for the m.p. H. Moissan said that when chromium is fused in the electric arc-furnace it forms a very fluid, bright liquid with the appearance and fluidity of mercury; and it can be cast in a mould. It can be distilled in the electric arc-furnace; and H. C. Greenwood gave 2200° for the **boiling point** of chromium—W. R. Mott estimated 3000°. J. Johnston gave for the **vapour pressure** $\log p = -14900T^{-1} + 8·91$; and

| | 980° | 1090° | 1230° | 1400° | 1610° | 1800° | 1890° | 2200° |
|---|---|---|---|---|---|---|---|---|
| $p$ | $10^{-3}$ | $10^{-2}$ | $10^{-1}$ | 1 | 10 | 50 | 100 | 760 |

F. Wüst and co-workers, and W. Herz gave 32·00 Cals. for the latent **heat of fusion** per gram; and S. Umino, 70·05 Cals. E. Kordes gave 0·91 (cals.) for the entropy of chromium. G. N. Lewis and co-workers gave 5·8 for the at. **entropy** of chromium at 25°; W. Herz, 10·85; and B. Bruzs, 19·8 at the m.p. E. D. Eastman and co-workers studied this subject; and R. D. Kleeman, the internal and free energy of chromium.

A. L. Bernoulli[4] gave 2·67 for the **index of refraction** of chromium, and 1·63

for the absorption coeff. for Na-light. H. von Wartenberg gave 2·97 for the index of refraction, $\mu$; 4·85 for the absorption coeff., $k$; and 69·7 per cent. for the **reflecting power,** $R$. V. Fréedericksz gave

| | | | | | | |
|---|---|---|---|---|---|---|
| $\lambda$ | 257$\mu\mu$ | 325$\mu\mu$ | 361$\mu\mu$ | 444$\mu\mu$ | 502$\mu\mu$ | 668$\mu\mu$ |
| $\mu$ | 1·641 | 1·259 | 1·530 | 2·363 | 2·928 | 3·281 |
| $k$ | 3·69 | 2·91 | 3·21 | 4·44 | 4·55 | 4·30 |

W. W. Coblentz and R. Stair, and W. W. Coblentz gave for the **reflecting power**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\lambda$ | 0·5$\mu$ | 1·0$\mu$ | 2·0$\mu$ | 3·0$\mu$ | 4·0$\mu$ | 5·0$\mu$ | 9·0$\mu$ |
| $R$ | 55 | 57 | 63 | 70 | 76 | 81 | 92 per cent. |

P. R. Gleason, W. W. Coblentz and R. Stair, and M. Luckiesh made observations on the subject. V. Fréedericksz gave 60 to 72 per cent. for $\lambda$=257$\mu\mu$ to 668$\mu\mu$. F. J. Michéli observed no difference between the reflecting power of passive and active chromium, although in the case of passive and active iron, the results indicated that a film was formed. A. L. Bernoulli found that the results of F. J. Michéli were anomalous owing to gas absorption, for there is a marked difference in the reflecting powers of the active and passive forms of chromium—this is attributed to the presence of a surface film on the passive metal. J. H. Gladstone found the **refraction equivalent** of chromium to be 15·9; and the **specific refraction,** 0·305. W. J. Pope gave 22·25 for the refraction eq. of tervalent chromium. T. Bayley,[5] and M. N. Saha discussed the colour relations of chromium and of copper, manganese, iron, cobalt, and nickel; and J. Piccard and E. Thomas, of chromous and chromic ions, and of chromates and dichromates. W. Biltz discussed the relation between colour and the magnetic properties of the element.

Chromium compounds do not give the ordinary **flame spectrum.** V. Merz[6] said that when a chromate moistened with sulphuric acid is introduced at the edge of the colourless gas flame, the edge of the flame acquires a dark reddish-brown colour and a rose-red mantle which can be recognized with 0·001 mgrm. of the chromate. K. Someya observed that the colourless soln. obtained by reducing a very dil. soln. of potassium dichromate shows that chromous ions are colourless, and that thiocyanate produces the blue colour of conc. soln. owing to the formation of complex ions. F. Gottschalk and E. Drechsel found that the vapour of chromyl chloride in the oxy-coal gas flame shows a band spectrum in the green and yellow. A. Gouy found that when chromium salts are fed into the bunsen flame, the inner cone shows some spectral lines. J. N. Lockyer also found spectral bands with chromium salts in the oxy-coal gas flame, and G. D. Liveing and J. Dewar observed

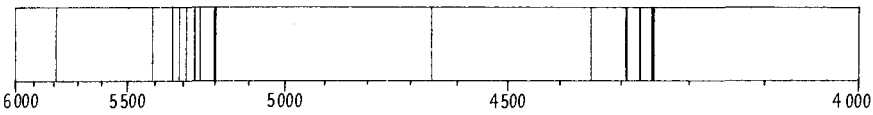


FIG. 3.—Spark Spectrum of Chromium.

numerous lines in the specimen of the explosion flame of electrolytic gas with chromium salts. W. N. Hartley observed the oxy-hydrogen flame spectrum. H. W. Vogel, M. A. Catalan, and C. de Watteville studied this subject. G. Kirchhoff first investigated the **spark spectrum,** and he was followed by W. A. Miller, W. Huggins, R. Thalén, C. C. Kiess, A. Mitscherlich, L. de Boisbaudran, G. Ciamician, J. Parry and A. E. Tucker, G. D. Liveing and J. Dewar, J. N. Lockyer, F. McClean, E. Demarçay, L. and E. Bloch, A. de Gramont, W. E. Adeney, R. J. Lang, O. Lohse, F. Exner and E. Haschek, R. E. Loving, A. Hagenbach and H. Konen, M. A. Catalan, J. H. Pollock, J. H. Pollock and A. G. G. Leonhard, F. L. Cooper, J. M. Eder and E. Valenta, and H. Smith. The simple spark spectrum shown by, say, a soln. of chromic chloride is characteristic, and can be employed in the spectroscopic detection of chromium, Fig. 3. There is the 5207-line in the green; and a group of three

lines 4290, 4275, and 4254 in the indigo-blue, which are well defined, while there are feebler lines 4345 in the blue; 5253, 5276, 5297, 5341, and 5410 in the green; and 5790 in the orange-yellow. E. O. Hulburt studied the spectrum of the condensed spark in aq. soln. The **arc spectrum** of chromium was studied by J. N. Lockyer, B. Hasselberg, F. Exner and E. Haschek, M. A. Catalan, H. Gieseler, Lord Blythwood and W. A. Scoble, R. Frerichs, A. S. King, A. B. McLay, J. Clodius, D. Foster, L. Stüting, K. Burns, S. P. de Rubies, J. Buchholz, C. C. Kiess. C. C. Kiess and W. F. Meggers, and J. Hall. The **ultra-violet spectrum** was studied by W. A. Miller, J. C. McLennan, A. B. McLay, R. A. Millikan and I. S. Bowen, V. Schumann, F. Exner and E. Haschek, L. and E. Bloch, W. E. Adeney, M. Edlen and M. Ericson, and R. Richter; the **ultra-red spectrum,** by K. W. Meissner, T. Dreisch, and H. M. Randall and E. F. Barker. H. Finger examined the effect of the *medium* on the lines in the spark spectrum; F. Croze, M. A. Catalan, and A. de Gramont, *les raies ultimes*, and *les raies de grand sensibilité;* G. D. Liveing and J. Dewar, the *reversed lines* in metal vapours; J. N. Lockyer and F. E. Baxandall, M. Kimura and G. Nakamura, and J. N. Lockyer, the *enhanced lines;* A. S. King, and H. Geieler, the *anomalous dispersion;* W. J. Humphreys, the effect of *pressure;* J. A. Anderson, and H. Nagaoka and Y. Sugiura, the **Stark effect** or the influence of an *electric field* on the arc spectrum; and A. Dufour, H. du Bois and G. J. Elias, W. Miller, J. E. Purvis, C. Wali-Mohammad, O. Lüttig, W. C. van Geel, E. Krömer, and W. Hartmann, the **Zeeman effect.** The **absorption spectrum** of the vapour was examined by J. N. Lockyer and W. C. Roberts-Austen, R. V. Zumstein, H. D. Babcock, A. S. King, A. W. Smith and M. Muskat, H. Gieseler and W. Grotrian, and W. Gerlach; the absorption spectrum of aq. soln. of various salts (*q.v.*) was examined by W. de W. Abney and E. R. Festing, W. Ackroyd, T. Bayley, H. Becquerel, W. Böhlendorff, H. Bremer, D. Brewster, A. Byk and H. Jaffe, T. Carnelley, S. Kato, H. Croft, T. Erhard, A. Étard, J. Formanek, J. Gay, J. H. Gladstone, F. Hamburger, A. Hantzsch, A. Hantzsch and R. H. Clark, W. N. Hartley, J. M. Hiebendaal, H. C. Jones and W. W. Strong, G. Joos, B. Käbitz, O. Knoblanch, W. Lapraik, H. Fromherz, G. D. Liveing and J. Dewar, G. Magnanini, G. Magnanini and T. Bentivoglio, F. Melde, W. A. Miller, H. Moissan, J. Müller, E. L. Nichols, C. Pulfrich, A. Recoura, G. B. Rizzo. P. Sabatier, C. A. Schunck, H. Settegast, C. P. Smyth, J. L. Soret, G. J. Stoney and J. E. Reynolds, H. F. Talbot, H. M. Vernon, K. Vierordt, E. Viterbi and G. Krausz, H. W. Vogel, E. Wiedemann, and C. Zimmermann; and the absorption lines in the spark spectrum under water, by E. O. Hulburt. J. Formanek said that the chromium salts do not react with alkanna tincture. L. de Boisbaudran examined the **fluorescence spectrum.** According to T. Tanaka, chromium is the principal agent in the cathodoluminescence of corundum. No **series spectrum** has been observed with chromium, but the lines have been studied from this point of view by L. Janicki, A. Dufour, P. G. Nutting, H. N. Russell, S. Goudsmit, E. Krömer, M. Steenbeck, H. Deslandres, A. Sommerfeld, H. E. White, H. E. White and R. C. Gibbs, M. A. Catalan, R. Mecke, H. Gieseler, R. Frerichs, R. J. Lang, C. V. Ramon and S. K. Datta, G. Wentzel, Y. M. Woo, C. Wali-Mohammed, H. Pickhan, C. C. and H. Kiess, A. de Gramont, O. Laporte, W. F. Meggers and co-workers, A. E. Ruark and R. L. Chenault, C. C. Kiess and O. Laporte, R. J. Lang, M. A. Catalan, C. E. Hesthal, and N. Seljakoff and A. Krasnikoff.

B. Rosen,[7] M. Levi, and G. Kettmann studied the **X-ray spectrum.** The K-series in the X-ray spectrum was studied by V. Dolejsek, V. Dolejsek and K. Pestrecoff, B. C. Mukherjee and B. B. Ray, M. Steenbeck, C. G. J. Moseley, W. Duane and co-workers, D. Coster, G. Wentzel, N. Selijakoff and A. Krasnikoff, E. C. Unnewehr, A. E. Lindh, H. Fricke, S. Eriksson, T. L. de Bruin, W. Bothe, B. Kievit and G. A. Lindsay, F. Wisshak, S. Pastorello, J. H. van Vleck and A. Frank, H. Beuthe, H. R. Robinson and C. L. Young, N. Seljakoff and co-workers, M. J. Druyvesteyn, R. C. Gibbs and H. E. White, F. Hjalmar, K. Chamberlain, O. Stelling, M. Siegbahn

and co-workers, B. Walter, J. Schrör, and H. Stensson. There are the lines $\alpha_2\alpha' = 2{\cdot}28855$; $\alpha_1\alpha = 2{\cdot}28517$; $\alpha_3\alpha_4 = 2{\cdot}2733$; $\beta_1\beta = 2{\cdot}08144$; and $\beta_2\gamma = 2{\cdot}069$. The L-series was examined by J. Schrör, A. Duvanlier, C. E. Howe, F. de Boer, F. P. Mulder, G. Kellström, F. L. Hunt, and R. Thoroeus; the M-series, by F. P. Mulder, and B. C. Mukherjee and B. B. Ray; the N-series, by F. P. Mulder; and the O-series, by F. P. Mulder.

U. Andrewes and co-workers [8] studied the absorption of **X-rays.** The absorption coefficients of X-rays from chromium radiator were studied by U. Andrewes and co-workers, D. M. Bose, C. G. Barkla and C. A. Sadler, and T. E. Aurén. O. W. Richardson and F. S. Robertson investigated the soft X-rays from chromium. A. C. Davies and F. Horton gave the critical potentials for soft X-rays. J. C. McLennan, and M. A. Catalan gave 6·7 volts for the **ionization potential,** and 2·89 volts for the first **resonance potential.** H. N. Russell gave 6·74 volts for the first ionization potential and 16·6 volts for the second. B. B. Ray and R. C. Mazumdar discussed the critical potential; E. Rupp, the deflection of electrons by films of chromium; and R. H. Ghosh, and B. B. Ray and R. C. Mazumdar, the relation between the ionizing potential and the electronic structure. E. Rabinowitsch and E. Thilo studied the subject. J. E. P. Wagstaff gave $8{\cdot}3\times10^{12}$ for the **vibration frequency;** and W. Herz, $8{\cdot}43\times10^{12}$. According to R. Whiddington, the critical velocities of cathode rays required to excite K- and L-radiations with the chromium radiator are respectively $5{\cdot}0\times10^{9}$ and $2{\cdot}0\times10^{8}$ cm. per sec. E. C. Unnewehr studied the dependence of the energy of emission of the K-radiation on the applied voltage. The use of chromium as a radiator for X-rays was discussed by R. Whiddington, and C. A. Sadler and A. J. Steven. A. Wehnelt classed chromic oxide as an "inactive oxide" so far as the emission of electrons is concerned, when it is fixed on a platinum disc and used as a cathode of a discharge tube; but A. Poirot found that **anode rays** are emitted from chromium. W. Espe studied the subject. E. Rupp discussed the passage of electrons through thin films of chromium. P. Weiss and G. Foex calculated values for the **atomic moments;** O. W. Richardson and F. S. Robertson studied the **photoelectric effect,** and U. Nakaya examined the influence of adsorbed gas on this phenomenon. R. E. Nyswander and B. E. Cohn studied the thermo-luminescence of glass activated with chromium.

P. E. Shaw and C. S. Jex [9] said that chromium acquires negative **triboelectricity** when rubbed on glass. K. F. Herzfeld discussed the metallic conductivity of chromium. I. I. Shukoff gave $38{\cdot}5\times10$ mhos for the **electrical conductivity** of chromium at 0°; and A. Schulze gave $2{\cdot}60\times10^{-6}$ for the sp. resistance at 0°. J. C. McLennan and C. D. Niven gave for the sp. resistance, $R$, of aged and unaged chromium:

| | | 29° | 27° | −152·4° | −193° | −190° | −268·8° | −269·99° | −270·8° |
|---|---|---|---|---|---|---|---|---|---|
| $R$ | aged | 17·2 | — | 0·90 | 2·01 | — | — | — | — |
| | unaged | — | 43·8 | 27·0 | — | 28·8 | 26·7 | 26·6 | 26·5 |

They observed no indication of superconductivity at low temp. P. W. Bridgman gave $-5{\cdot}8\times10^{-7}$ for the press. coeff. of the resistance; and 0·000033 for the temp. coeff., the resistance at 30° being $160\times10^{5}$. The values are taken to represent an impure metal. J. C. McLennan and co-workers found for the resistance of aged chromium, at different temp. absolute, to be:

| | 292° | 273° | 80° | 20·6° | 4·2° | 2·25° K. |
|---|---|---|---|---|---|---|
| $R\times10^{3}$ | 5·59 | — | 0·655 | 0·260 | 0·258 | 0·258 ohms |
| Sp. resistance | 17·2 | 15·25 | 2·01 | 0·80 | 0·79 | 0·79 |

The values of the ratio $R/R_0$ at liquid air temp. is 0·132, and at liquid hydrogen temp., 0·059. P. Kapitza examined the effect of a magnetic field on the electrical conductivity. Z. A. Epstein compared the electrical conductivities of the elements and their position in the periodic table. K. Hopfgartner found that the transport numbers of the chromic ion in hydrochloric acid soln., are 0·318, 0·357, and 0·414 respectively for 1·00, 0·32, and 0·075 eq. soln.—*i.e.* for zero concentration, 0·446.

The mobility of the chromic ion is 46·3 to 53. It is assumed that the chromic ion is surrounded by a fairly large water-sheath. E. Newbery discussed the over-voltage; S. J. French and L. Kahlenberg, the gas-metal electrodes obtained by chromium and oxygen, nitrogen, or hydrogen; and N. Koboseff and N. I. Nebrassoff, the cathodic polarization.

According to J. J. Berzelius, there are two allotropic forms of chromium. The one, **α-chromium,** obtained as a grey metallic powder by reducing chromium trichloride with potassium, inflames between 200° and 300° and burns vividly to chromic oxide, and it dissolves readily in hydrochloric acid with the evolution of hydrogen; the other, **β-chromium,** obtained by reduction with carbon at a high temp., cannot be oxidized by heat, by boiling with aqua regia, by hydrofluoric acid, or by ignition with potassium hydroxide or nitrate. He added that corresponding modifications can be traced through many of the compounds of chromium; but this statement is not now regarded as correct because certain allotropic forms of the salt are now explained without assuming that they are due to allotropic forms of the element. As indicated above, R. Bunsen asked if the electrolysis of soln. of the green and violet chromium salts would give corresponding allotropic forms of the element, but the answer is in the negative. W. Hittorf recognized that chromium can exist in an active and in a **passive state.** Chromium is active in contact with hydrofluoric, hydrochloric, hydrobromic, hydriodic, acetic, oxalic, sulphuric, and hydrofluosilicic acids, that is, the metal dissolves in these acids with the evolution of hydrogen, if the acids are concentrated and cold, and if the acids are dilute, application of heat may be required. On the other hand, chromium is passive in chlorine or bromine water, in conc. nitric, chromic, phosphoric, chloric, perchloric, citric, formic, or tartaric acid, for the metal does not dissolve therein. The difference in its behaviour towards these acids is associated with a difference in the electrode potential of chromium for the difference in the e.m.f. of the two states amounts to about 1·6 volts, for with active chromium, the e.m.f. of the cell Cr/acid, $H_2CrO_4$/Pt is about 1·9 volt, and with the passive metal, 0·3 volt. In the electrochemical series, active chromium is close to zinc, but passive chromium stands near platinum. Otherwise expressed, passive chromium behaves as a noble metal, being electronegative towards zinc, cadmium, iron, nickel, copper, mercury, and silver, for it does not decompose even boiling soln. of these salts, excepting that it reduces mercuric and cupric salts respectively to mercurous and cuprous salts. When chromium is employed as anode in soln. in which it is indifferent, it becomes covered with a yellow film of chromic acid, and the loss of weight of the anode was found to correspond with the production of sexivalent chromium ions; this occurs even in soln. of hydrogen chloride in which chromium ordinarily dissolves with the formation of chromous salts. This may be due either to the decomposition of the water by the anion and subsequent formation of chromic acid from the liberated oxygen, or to the formation of a compound of sexivalent chromium with the anion and the decomposition of this compound by water; no such compound, however, is actually known to exist. In soln. of potassium thiocyanate or of an iodide, the chromium anode experiences no loss. The coeff. of the amalgamated metal M in the cell M | KCl, $NaNO_3$, $AgNO_3$ | Ag at 5° are:

| M | . | Zn | Cd | Pt | Fe | Sn | Cu | Cr |
|---|---|---|---|---|---|---|---|---|
| Volt | . | 1·534 | 0·974 | 1·123 | 0·955 | 1·010 | 0·689 | 0 |

W. J. Müller found that there are certain current densities which vary with the time required to make the metal passive. W. Muthmann and F. Fraunberger found the electrode potential between chromium and *N*-KCl against the normal calomel electrode zero to be −0·63 volt for the most active metal, and +1·19 volt for the most passive. Fresh electrolytic chromium was found by B. Neumann to be strongly active. W. Muthmann and F. Fraunberger observed variations of the electrode potential with the same piece of metal. A piece 25 cms. long had a potential of −0·03 volt at one end, and +0·03 at the other; and when activated,

—0·17 volt and —0·07 volt. W. Rathert observed that a piece of chromium polished in air had a potential against 0·1*N*-$H_2SO_4$ of +0·26 volt, and after lying some time in air, +0·37 volt; and when polished, in hydrogen, —0·054 volt at first, and +0·071 after standing 3 minutes in the liquid. Thus, polished chromium is not active in hydrogen. Passive chromium becomes active when it is charged electrolytically with hydrogen; but molecular hydrogen has scarcely any action on the potential of a passive chromium electrode. A. M. Hasebrink observed that when chromium is treated with nitric acid, and heated in nitrogen, it remains active a few hours, and then becomes passive; if hydrochloric acid be substituted for nitric acid, the chromium remains active as long as it is kept in nitrogen. Chromium activated in hydrogen remains active in this gas. At ordinary temp., nitrogen, hydrogen, and carbon dioxide do not activate chromium, nor do they passivate chromium made active by scratching. Occluded gases influence the rate of activation or passivation of chromium. Oxygen favours passivation, hydrogen retards it. Atm. oxygen rapidly passivates chromium; iodine acts as an activating agent, never as a passivating agent. The potential of chromium or nickel rubbed with emery in an indifferent atm., falls at first, then recovers partially; and after repeated rubbings, a constant potential is finally reached which is lower than the initial one. Molecular oxygen passed through an electrolyte, during the electrolysis of chromium, raises its potential; but the potential is scarcely affected if hydrogen or nitrogen be employed in place of oxygen. Electrolytic oxygen or hydrogen affect the potential enormously. The subject was discussed by T. Murakami, and B. Strauss and J. Hinnüber.

As previously indicated, chromium becomes passive when treated with certain oxidizing agents—*e.g.* chlorine or bromine-water, soln. of iodine and potassium iodide, conc. nitric and chromic acids, chloric acid, potassium permanganate, potassium ferricyanide, ferric chloride, and oxygen or air—N. Isgarischeff and A. Obrutscheva also found that oxidizing agents—like chromic acid, hydrogen dioxide, potassium permanganate—and exposure to air or to electrolytic oxygen make the metal passive; and, according to A. L. Bernoulli, the action of a soln. of quinine in benzene. Chromium also becomes passive when used as anode in an electrolytic cell. J. Alvarez found the strength of the current necessary to produce the passive state—the *critical strength of current*—depends on the conc. and temp. of the electrolyte. Thus, with 2·8*N*-, 0·7*N*-, and 0·175*N*-HCl, the critical voltages were 0·35, 0·085, and 0·034 volt respectively; and with 5*N*-, 0·6*N*-, and 0·075*N*-$H_2SO_4$, respectively 0·098, 0·046, and 0·018 volt. C. Fredenhagen applied a gradually increasing or decreasing e.m.f. to a chromium electrode immersed in sulphuric acid, and determined the electrode potential and the strength of the polarization current. The electrode potential at the point where activity or passivity sets in is not well-defined, and this is taken to support the hypothesis that passivity does not depend on the formation of an oxide film or of another modification of the metal, but is rather related to the rate at which the metal becomes charged with oxygen. The electrode potential attained when passivity or activity sets in is very sensitive to slight changes in the conc. of the acid; and a rise of temp. favours the active state. The passive condition is said to be attained when the oxygen polarization extends uniformly over the whole surface of the electrode; and the appearance of the active state when the polarization e.m.f. is lowered is due to the fact that the reactions which use up oxygen begin to overbalance those which produce oxygen. According to W. Rathert, the potential at which the passive metal becomes active is not the same as that at which the active metal becomes passive, and that the abrupt change observed by F. Flade does not represent a boundary potential below which the metal is active and above which it is passive. The metal may be active or passive on both sides of this point depending on its previous treatment. U. Sborgi and G. Cappon found that chromium in an ethyl alcohol soln. of calcium nitrate and ammonium nitrate is passive with low-current densities, and with high-current densities chromium salts

are formed. E. Becker and H. Hilberg found that the maximum distance for establishing contact with a metal surface is slightly greater for passive than for active chromium.

According to W. Hittorf, and A. Meyer, and as indicated above, passive chromium is activated by soln. of hydrofluoric acid and of a number of other acids —*e.g.* hydrochloric, hydrobromic, hydriodic, sulphuric, and oxalic acids—by the halogens, and by raising the temp. The more dil. the acid, the higher the temp. necessary for activation; hydrogen is evolved, and chromous salts are formed. Soln. of the chlorides of the alkaline and alkaline earths act at a higher temp.; soln. of potassium bromide, cupric chloride or palladium dichloride do not act at 100°. The molten fluorides, chlorides, bromides, and iodides are good activating agents, and A. L. Bernoulli observed that chromium is activated when heated with benzene, toluene, naphthalene, and anthracene; and, according to N. Isgarischeff and A. Obrutscheva, when the surface is mechanically purified. The metal is activated by using it as cathode with indifferent acids like formic, citric, or phosphoric, *i.e.* by electrolytic reduction. The current required is greater the more dil. the soln., and the lower the temp. According to G. C. Schmidt, passive chromium becomes active by disturbing the surface, by scratching, knocking, and so on, but in nitric acid it remains permanently passive. Activated chromium placed in dil. hydrochloric or sulphuric acid remains permanently active. On removal from the acid, however, it becomes passive again after a short time, even although oxygen is rigorously kept away. Chromium heated in a vacuum or in nitrogen is active. In hydrochloric acid at 100° it is also active, and at this temp. chlorine. bromine, and iodine attack chromium and activate it, solely because the surface is disturbed. H. Eggert observed that chromium remains active in dry hydrogen, or nitrogen, but becomes passive if oxygen be present or if it be exposed to air. W. Rathert found that passive chromium becomes active when it has absorbed hydrogen ions by diffusion, and it then dissolves electrolytically in accord with Faraday's law. U. Sborgi and A. Borgia observed that a magnetic field had no influence.

Active chromium is indifferent towards water, but in strong acids it dissolves forming chromous salts, and in weak acids it dissolves when it is the cathode in an electrolytic cell, producing chromous salts: $Cr+2HCl=CrCl_2+H_2$. The dissolution of a chromium anode to form bivalent chromium ions is then in accord with Faraday's law so that $1Ag=\frac{1}{2}Cr$. The highest numerical value for the electrode potential observed by W. Muthmann and F. Fraunberger is —0·63 volt with $N$-KCl; B. Neumann observed —0·535 volt with chromic sulphate; —0·518 volt with chromic chloride; and —0·516 volt with chromic acetate; and W. Rathert obtained with $N$-$Cr_2(SO_4)_3$, —0·395 volt, and with $0{\cdot}1N$-$H_2SO_4$, —0·491 volt. The potential of the active metal towards normal soln. of $Cr^{\cdot\cdot}$-ions is —0·6 volt. N. Bouman gave —0·546 volt for chromium in $N$-$H_2SO_4$. This potential is independent of the metal on which the chromium is deposited, and also of the method of activation. It is also independent of the ratio of $Cr^{\cdot\cdot}$- to $Cr^{\cdot\cdot\cdot}$-ions in soln. It is curious that, with increasing hydrogen-ion concentration, the potential becomes more positive in sulphuric acid, but more negative in hydrochloric acid soln. Chromium remains active only when the acidity is above a certain limit, about $0{\cdot}001N$. A. H. W. Aten gave —0·75 volt, or, when referred to the hydrogen electrode, —0·47 volt. This active potential is attained only when sufficient hydrogen is present; hydrogen hastens the attainment of the electrode equilibrium. Active chromium can be anodically polarized in a soln. of potassium chloride without becoming passive. If the metal immersed in a soln. of chromous sulphate is anodically polarized with a sufficiently strong current, the chromium becomes passive, but when the current is interrupted, the potential of the metal is found to be more negative than before polarization. The passivation during anodic polarization and activation after this treatment are shown by chromium which has been deposited on copper, silver, or gold. The degree of activation after anodic polariza-

tion increases with the strength of the polarizing current. The resistance offered by the metal to the action of the polarizing current is greater when the strength of the current is gradually increased than when the current strength is increased rapidly. The resisting power of the metal is smaller when the chromium has been previously subjected to cathodic polarization. Active chromium reduces fused cadmium chloride, bromide, or iodide, and the chlorides of copper, silver, and lead; as well as hot soln. of copper, gold, palladium, and platinum, and it thereby becomes passive. Passive chromium, as indicated above, differs from active chromium in that it is covered with a surface film of some kind, and it then behaves like a noble metal, for it does not dissolve in nitric, chloric, or perchloric acid; it is indifferent towards neutral soln. of the salts of copper, silver, cadmium, mercury, and nickel—*vide supra*; and it does not reduce soln. of the chlorides of gold, palladium, or platinum. It then appears to be a nobler metal than copper, silver, or mercury. The presence or absence of a film was discussed by W. J. Müller, and J. Hinnüber. W. Muthmann and F. Fraunberger observed that the electrode potential in *N*-KCl may be as great as +1·19 volt. N. Bouman found that in the passive state, the potential of chromium in potassium chloride soln. depends on the previous treatment which it has received, and this is shown to be equally true of other metals, including platinum. Consequently, no conclusions can be drawn from such measurements relative to the state of the metal. The potential of passive chromium varies with the metal on which it is deposited. When chromium is polarized anodically, the potential varies in the same way with the acidity as the potential of the unattackable electrode. The polarization tension is therefore governed by the reaction $Cr^{\cdots}+3H_2O=CrO_3+6H^{\cdot}+3(+)$. When passive chromium dissolves at the anode it forms chromic acid, and the dissolution is in accord with Faraday's law provided $1Ag=\frac{1}{6}Cr$. Otherwise expressed, passive chromium dissolves as sexivalent chromium ions. R. Luther said that the anode potential is +0·6 volt and energy is required for the reaction symbolized: $Cr+4H_2O\rightarrow H_2CrO_4+3H_2O$, or $Cr+4H_2O+6(+)\rightarrow CrO_4^{\cdot\cdot}+8H^{\cdot}$. The active and passive states are mutually convertible one into the other by a suitable change in the conditions. Thus, W. Rathert found that with active chromium dipping in *N*-$Cr_2(SO_4)_3$, the electrode potential at the beginning was —0·395 volt, and in 2, 23, and 73 min. was respectively —0·359, —0·209, and —0·129 volt; and E. Grave found that passive chromium in 0·1*N*-KOH had an electrode potential of +1·895 volt at the beginning, after 20 sec. +1·176 volt, and after 1, 5, and 12 min. respectively +1·084, +0·981, and +0·925 volt. A. L. Bernoulli found that passive chromium is activated by aromatic hydrocarbons —benzene, toluene, *p*-xylene, naphthalene, and anthracene—and the changes in the e.m.f. are greater the more readily the hydrocarbon is oxidized. Active chromium becomes passive when treated with a boiling soln. of *p*-benzoquinone in benzene; and also by exposure to air. According to A. H. W. Aten, if chromium has been rendered passive by anodic polarization, in a soln. of potassium chloride, the active condition may be restored by heating the soln. This change occurs even when the polarizing current is continued during the heating of the soln. and on cooling, the chromium remains in the active condition, provided the current is not too strong. U. Sborgi and G. Cappon found that in an alcoholic soln. of calcium or ammonium nitrate, chromium shows passivity phenomena similar to those which occur in aq. soln.

W. Hittorf concluded that the passivity of chromium is not due to the formation of an oxide film, but rather to the metal assuming a different electrical state; the metal in the passive state is in a strained or coerced condition—*Zwangzustand*—so that instead of dissolving as a bivalent element it dissolves as a sexivalent element. The film hypothesis, discussed in connection with the passivity of iron, best fits the facts. C. W. Bennett and W. S. Burnham stated that the film is best regarded as a film of oxide which is rendered stable by adsorption into the metal. The oxide is usually unstable, but becomes stable when adsorbed by the

metal. The oxide is not higher than $CrO_3$, and is probably $Cr(CrO_4)$, or $CrO_2$, but in the further oxidation at the anode, the higher oxide $CrO_3$ is formed, and the chromium passes into soln. in the sexivalent state. A. L. Bernoulli gave $Cr_5O_9$, or $2Cr_2O_3.CrO_3$, for the composition of the film. The subject has been discussed by A. Adler, F. Flade, C. Fredenhagen, E. Grave, W. J. Müller and co-workers, W. Rathert, O. Sackur, H. Kuessner, E. Newbery, G. C. Schmidt, etc.—*vide* iron. N. Bouman favoured the allotropic theory. According to N. Isgarischeff and A. Obrutscheva, chromium shows no definite transition point at which it passes into the active state; the metal can become active at any temp.; the activation depends on the properties of the medium. This and the mode of formation of passive chromium show that the passivity of chromium is connected with the formation of a protecting oxide film on the surface. The protecting film is a transparent, colloidal substance, the density and permanence, and consequently the passivating action, of which depend on the nature of the medium, particularly on the presence of those ions, such as chloride- and bromide-ions, which bring about colloidal transitions. Chloride-ions have the greatest disturbing effect on the film, and make it permeable to most reagents. Particles of passive chromium become active when brought into contact with active chromium zinc, or magnesium. Since these metals are all more electro-negative than passive chromium, this action is due to the formation of a galvanic element which liberates hydrogen and consequently reduces the oxide film. The oxide film is also the cause of the anomalies of chromium. E. Liebreich and W. Wiederholt plotted the current density against the potential of electrolytic chromium in 1·02*N*-$K_2SO_4$. At high current densities, the chromium dissolves as chromate, at lower current densities and potentials, Fig. 4, the metal acquires a film of the chromic chromate and dissolves only slightly at a potential of about 0·5 volt, and a small current density, the potential gives a slight rise with falling current density and true passivity, owing to the insolubility of a film of hydroxide, sets in. The passivity persists when the metal is made a cathode at small current densities. The curve for a potential of 0·4 volt rises steeply as the metal dissolves to form chromous salts which are partially oxidized near the electrode forming secondary hydrogen: $2CrSO_4+H_2SO_4=Cr_2(SO_4)_3+H_2$. At higher current densities, and at about —0·5 volt, the metal dissolves forming hydrogen directly. G. Grube and co-workers found that with an active chromium electrode (prepared by cathodic polarization) with 0·02–0·2*N*-sulphuric and hydrochloric acid soln., the anode potential is found to increase suddenly when the anode current density reaches a certain value. This critical value increases with the conc. of the acid and with increasing temp. During the first stage, the chromium ions pass into soln. entirely in the bivalent condition, and, during the second stage, entirely in the sexivalent condition. At the ordinary temp., *N*-NaCl behaves similarly, but at higher temp. the current density-potential curves are of somewhat different form. H. Kuessner suggested that it is possible for chromium ions of varying valency to be formed simultaneously in soln. G. Grube and co-workers hold that chromium goes primarily into soln. as bivalent ions at lower current densities, and that these are immediately oxidized to the tervalent condition, whilst at higher current densities sexivalent ions are formed. The anode potential in *N*-, 4*N*-, 8*N*-, and 16*N*-potassium hydroxide soln. has also been studied at different temp.; for low current densities, the curve is discontinuous as in acid soln., and a similar explanation is adopted. In the alkaline soln., the anode becomes coated with a fine grey powder, which apparently consists

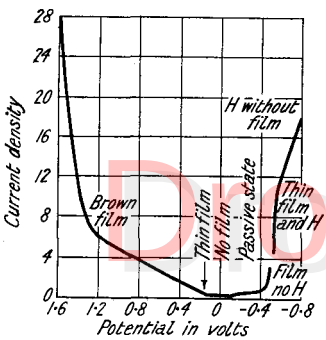


FIG. 4.—Current Density-Potential Curves of Chromium.

of a lower oxide of chromium. The facts support the oxide film theory of passivity. F. Krüger and E. Nähring found the X-radiograms of active and passive metal support the oxide-film theory. The subject was discussed by U. R. Evans. A. M. Hasebrink's chemical experiments favour the oxide film theory, but not the hydrogen theory, or the surface-tension theory of W. Hittorf, and G. C. Schmidt. L. McCulloch found cases of passivity with sparingly-soluble sulphate films.

A. S. Russell supposed that when in the active state, the atoms of chromium have two electrons in the fourth quantum orbit, and that when the metal becomes passive one of these electrons is removed to the third quantum orbit. The subject was studied by E. Müller, E. Liebreich, H. Eggert, and N. Isgarischeff and A. Obrutscheva. W. J. Müller and E. Noack found that with thermite chromium in $N$-$H_2SO_4$, so long as the current density falls below a certain critical value, $i_c$, which varied from sample to sample according to treatment, the metal remained active, and dissolved with the evolution of hydrogen. On exceeding this critical value, a fall of density immediately set in, during which the log of the density varied inversely as the time since the commencement of the fall, and after sufficient time complete passivity resulted. Log $i_c$ was inversely proportional to the temp. between 0° and 35°. The activity of the chromium was characterized by a potential of −0·34 volt, and passivity by zero potential, so that during the time of falling density, the metal remained active. In W. J. Müller's theory of the passivity of iron, the metal dissolves in the acid, but owing to the high mobility of the hydrogen ions, the anodic soln. becomes impoverished in these ; hence basic ferrous salt is formed and deposits on the electrode when the soln. becomes saturated, thus increasing the resistance and decreasing the current, causing complete passivity only when the covering is complete. With chromium, the chromous salt first formed by dissolution of the metal in the acid rapidly oxidizes to chromic salt (hydrogen being evolved), which hydrolyzes much more rapidly than the iron salts ; with high current densities (*e.g.* 1400 milliamp. per sq. cm.), the time required for passivity is only 0·3 sec. With perfectly clean metal the fall of current density is often suspended for a time and then occurs suddenly ; this is explained by the supersaturation of the soln. with regard to hydroxide, which would be possible only in the absence of impurities.

According to J. L. R. Morgan and W. A. Duff,[10] when two electrodes—one of chromium and one of platinum—are immersed in dil. sulphuric acid, the current passes freely when platinum is made the anode, but if chromium is made the anode no current passes through the cell. If the applied e.m.f. be gradually increased when chromium is the anode, no current passes until about 75 volts are attained ; if the increase is made so rapid that the current passes from chromium to platinum, or if the cell is broken down by the application of more than 75 volts, it is an asymmetrical resistance when platinum is the anode, whilst if chromium is the anode the current passes freely ; again, if too high an e.m.f. be applied to the platinum anode, another reversal occurs, and about 75 volts can again be stopped using chromium as anode. The chromium cell can also be used for the **rectification of alternating currents.** The phenomenon is attributed to the formation of a resistant film as in the case of the aluminium cell. W. Günther-Schulze studied the attraction of electrons for the $CrO_4$-ions. H. Nagaoka and T. Futagama studied the spluttering of chromium by the disruptive discharge in a magnetic field.

W. Ostwald found that when active chromium acts on acids, there is a **periodicity** in the rate of evolution of hydrogen. A piece of passive chromium rendered active by contact with cadmium under acid, was dissolved in 2$N$-HCl. The curve showing the rate of action is irregular for about 15 minutes, when it becomes periodic, the velocity rapidly increasing to a maximum and then falling more slowly to a minimum. The duration of each period increases during the progress of the reaction. Different forms of curve were obtained from different pieces of chromium ; and two pieces placed in the same acid were found to give a double summation curve showing that the periodicity lies in the metal and not in the acid. An increase in

the concentration of the acid causes an increase in the frequency of the periodic phenomena; the frequency is doubled by a rise of about 10°; the frequency is increased by the addition of oxidizing agents—*e.g.* nitric acid, nitrogen oxide, and chloric and bromic acids—and it is decreased by small amounts of formaldehyde or potassium cyanide. Dextrin and other carbohydrates help to bring about regular periodicity. No periodic phenomena were observed with the dissolution of iron, zinc, or manganese. The metal contained silicon, iron, sulphur, and carbon; but which of these is the active agent was not determined—purified chromium did not exhibit the phenomenon.

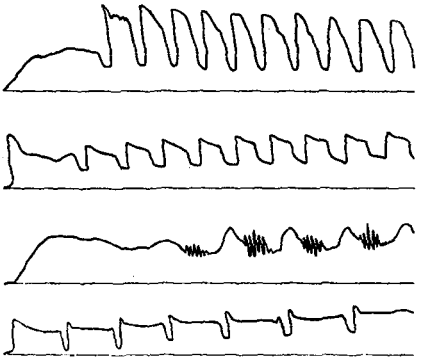

FIG. 5.—Periodic Evolution of Gas in the Dissolution of Chromium in Acids.

Nugatory attempts to render the metal active by the addition of cupric chloride, sodium sulphite, alcohol, ferrous chloride, ferric chloride, colloidal platinum, chromic acid, potassium nitrite; prolonged contact with metallic platinum; variation of temp. between 0° and 50°; previous treatment of the metal with chromic acid or potassium permanganate; fusion with potassium nitrate; heating on charcoal with sodium phosphate to give the metal a phosphorus content; melting in the electric oven in an atm. of coal-gas; using the metal as anode have all been made.

E. Brauer observed that the active chromium dissolving not only exhibits changes in its rate of evolution of hydrogen, but it also shows changes in its electric potential for the current produced by a cell of active chromium and platinum immersed in acid also varies periodically. The two sets of curves were analogous, but in some cases there is a variation in the electric properties when the evolution of hydrogen is apparently constant. The frequency increases with increasing conc. of acid, and is no longer apparent when the conc. of the acid is great enough. In one case, no periodicity was observed at 6°, periodicity was marked at 20°, and very pronounced at 31°. A piece of inactive chromium became active when rubbed with a piece of cadmium; and a slight activity was induced by the addition of arsenic or arsenic sulphides to the acid. E. Brauer attributes the periodicity to variations in the e.m.f. associated with the different oxidation stages of chromium. E. S. Hedges and J. E. Myers found that the addition of litharge would make chromium show the periodic phenomenon; they also showed that the periodic phenomenon is not due to the supersaturation of soln. or metal with gas; but is rather connected with the chemical change itself. The periodicity was shown to depend on the presence of a suitable catalytic agent and to be independent of the dissolving metal. The phenomenon was studied by B. Strauss and J. Hinnüber. W. Ogawa studied the action of chromium salts on galena as a radio-detector.

According to M. Faraday,[11] chromium is non-magnetic; this was not the conclusion of W. F. Barrett, but F. Wöhler, E. Glatzel, and H. Moissan found that the purified metal is non-magnetic. S. Curie studied the magnetization of iron with 2·5 to 3·4 per cent. of chromium; and K. Honda, of chromium with 20 per cent. of iron. M. Owen gave for the **magnetic susceptibility** of chromium $3{\cdot}16\times10^{-6}$ mass units; K. Ihde, $26\times10^{-6}$ vol. unit; and K. Honda, $3{\cdot}7\times10^{-6}$ mass unit at 18°, and $4{\cdot}2\times10^{-6}$ mass units at 1100°. J. Weiss and H. K. Onnes found that at −25·9°, the magnetic properties of chromium are very feeble. E. Wiedemann found that the atomic magnetism of chromium in various salt soln. approximates 42 when that of iron in ferric chloride is 100. This result is independent of the nature of the anion associated with the chromium. W. Lepke found that with a

field strength of $H$ kgrms., the magnetic susceptibilities $\times 10^{-6}$ mass unit of massive and powdered chromium, are :

| $H$ . | 1·0 | 3·3 | 7·0 | 10·0 | 16·0 | 18·0 |
|---|---|---|---|---|---|---|
| Mass. | 4·1 | 3·6 | 3·5 | 3·5 | 3·5 | 3·5 |
| Powd. | 4·3 | 5·4 | 4·2 | 4·1 | 4·0 | 3·9 |

P. Weiss and P. Collet calculated $63{\cdot}3\times10^{-6}$ for the atomic permeability. J. Safranek found the magnetic susceptibility of chromium to be independent of the magnetic field between 2000 and 14,000 gauss and of the temp. between 100° and 600° and to have a value of $4{\cdot}31\times10^{-6}$. The reciprocal of the susceptibility of the alloys plotted against temp. gives a straight line becoming concave towards the temp. axis at higher temp. The various magnetic constants are linear functions of the composition. P. S. Epstein found that the magnetic susceptibility of bivalent chromium is $7{\cdot}9\times10^{-4}$ per unit mass ; and of tervalent chromium, $5{\cdot}0\times10^{-4}$. Observations on the magnetic properties of chromium were also made by E. Wedekind, D. M. Bose, A. Dauvillier, R. H. Weber, and E. Feytis. P. Kapitza's observations on the effect of strong magnetic fields on the conductivity are summarized in Fig. 6. L. Rosenfeld discussed the relation between the magnetic susceptibility and the refractive index ; and E. C. Stoner, the magnetic moment. P. Weiss, and L. A. Welo studied the magnetism of chromium salts.

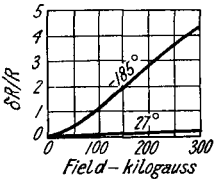


FIG. 6.—The Effect of Magnetic Fields on the Electrical Conductivity.

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## § 5. The Chemical Properties of Chromium

H. Moissan [1] studied the chemical affinity of chromium and the iron family of elements. F. Fischer and F. Schrötter observed no reaction when chromium is sparked beneath liquid **argon.** H. R. Carveth and B. E. Curry found that electrodeposited chromium can occlude about 250 times its vol. of hydrogen ; in one experiment 24·6 c.c. of the gas were obtained from 0·698 c.c. of metal. E. Martin measured the occlusion of hydrogen by chromium. According to G. F. Hüttig and F. W. Brodkorb, electrolytic chromium deposited at —50° may contain 0·45 per cent. of hydrogen, in supersaturated solid soln. At the ordinary temp., the hydrogen press. of this chromium is less than 1·0 mm., but at 58° a sudden evolution of hydrogen takes place, although a temp. of 350° is required in order to remove the whole of the gas. No reproducible relations between temp., press., and hydrogen conc. could be established. T. Weichselfelder and B. Thiede obtained **chromium trihydride,** $CrH_3$, as a black precipitate, by the action of hydrogen on an ethereal soln. of phenylmagnesium bromide. $C_6H_5MgBr$, in which the dry metal chloride is suspended. The sp. gr. is 6·77. W. Biltz discussed the mol. vol. According to H. Gruber, a sheet of electrolytically-deposited chromium will slowly evolve occluded hydrogen if placed in boiling water, and if held in a Bunsen flame it will appear to take fire and burn on the surface with a pale blue non-luminous flame, although the metal remains sufficiently cool to avoid being oxidized. A. Sieverts and A. Gotta studied this subject. The heat of formation of chromium hydride is 3800 cals. per mol. of hydrogen ; and the sp. gr. is 6·7663 to 6·7708.

A. L. Bernoulli said that chromium absorbs oxygen from **air** and so acquires the surface film of oxide. The behaviour of chromium in air depends on its state of subdivision ; there is pyrophoric chromium ; the specimen obtained by L. N. Vauquelin slowly oxidized when heated in air ; that obtained by A. Binet du Jassonneix glowed like tinder in **oxygen** at 300° ; that obtained by F. Wöhler when heated in air became yellow, then blue, and finally acquired a crust of green chromic oxide ; and that obtained by H. Moissan was unaltered by exposure to dry air, but in moist air the well-polished surface acquired a slight tarnish, owing to the formation of a superficial film which does not penetrate deeper into the metal. This subject was discussed by N. B. Pilling and R. E. Bedworth. H. P. Walmsley examined the nature of the sesquioxide obtained as smoke from the chromium arc. Unlike molybdenum, chromium was found by C. Matignon and G. Desplantes not to be oxidized when the finely-divided metal is shaken up with aq. ammonia in air. When heated by the tip of the oxyhydrogen blowpipe flame, chromium burns yielding brilliant sparks ; and when heated to 2000° in oxygen. it burns with the production of numerous sparks, more brilliant than those of iron. N. B. Pilling and R. E. Bedworth studied the rate of oxidation of chromium. F. Wöhler observed that chromium gives sparks and burns to chromic oxide when heated by the flame of a spirit-lamp fed with oxygen. H. W. Underwood described the use of chromium as an oxidation catalyst. H. V. Regnault, and F. Wöhler found that it decomposes when heated to bright redness in the vapour of **water,** forming hydrogen, and chromic oxide ; and J. J. Berzeiius found that the metal is not oxidized by boiling water. The action of **hydrogen dioxide** was found by L. J. Thénard to be at first feeble but later more vigorous. Part of the oxygen is given off free, and part combines with the metal. W. Guertler and T. Liepus observed no reaction by 48 hrs.' exposure to sea-water, aerated sea-water, or aerated rain-water. W. G. Mixter observed that no perchromate is formed by the action of **sodium dioxide** on chromium.

According to F. Wöhler, chromium glows when heated in **chlorine,** forming violet chromic chloride; and H. Moissan said that the reaction occurs at 600°. The red-hot metal is also attacked by **bromine** vapour—*vide infra*, chromic bromide; and with **iodine** vapour.' W. Hittorf observed that chlorine and bromine make chromium passive, while R. Hanslian found that the presence of chromium does not affect the f.p. or b.p. of iodine. G. Tammann studied the action of iodine vapour on chromium. W. Guertler and T. Liepus observed no reaction with 48 hrs.' exposure to sat. chlorine-water. C. Poulenc found that **hydrogen fluoride** converts the red-hot metal into chromous fluoride; and C. E. Ufer observed that with **hydrogen chloride,** chromous chloride is formed. J. J. Berzelius found that the metal dissolves in **hydrofluoric acid,** particularly when warm, and hydrogen is given off. F. Wöhler, E. Jäger and G. Krüss, J. J. Berzelius, H. St. C. Deville, etc., noted that the metal dissolves in **hydrochloric acid** with the evolution of hydrogen and the formation of chromous chloride. W. Guertler and T. Liepus observed no reaction in less than 8 hrs. with 10 and 36 per cent. hydrochloric acid—*vide supra*, the passive state. H. Moissan said that hydrochloric acid attacks the metal slowly in the cold, and rapidly when heated, while the dil. acid has no action at ordinary temp., but on boiling, the attack is vigorous. W. Rohn found that 10 per cent. hydrochloric acid dissolves 77·4 grms. per sq. dm. per hr. during 24 hrs. in the cold and 150 grms. per sq. dm. per hr. when hot; and D. F. McFarland and O. E. Harder, that the normal acid dissolves 16,976·4 mgrms. per week per sq. in. W. Hittorf observed that chromium dissolves in hydrofluoric and hydrochloric acids as well as in **hydrobromic acid and hydriodic acid,** forming chromous salts and hydrogen. T. Döring said that the less pure the chromium prepared by the alumino-thermite process, the more quickly is it dissolved by the halide acid. The chromous chloride formed by the soln. of chromium in hydrochloric acid is converted, by a secondary reaction, into chromic chloride, the change being complete if the reaction is carried out at the ordinary temp., but less than complete if at 100°. This change is ascribed to a catalytic action of silica. If air is excluded, chromous chloride is stable in neutral soln., but in hydrochloric acid soln. it has a tendency to form chromic chloride; the reaction, which is accompanied by evolution of hydrogen, is extremely slow, but is markedly accelerated by addition of platinum black, finely-divided gold, or silica. The formation of chromic chloride from chromous chloride in acid soln. takes place according to the equation: $2CrCl_2+2HCl \rightleftharpoons 2CrCl_3+H_2$. and is a reversible reaction. W. Hittorf found that chromium becomes passive in **chloric acid,** and in **perchloric acid.**

H. Moissan observed that chromium filings become incandescent if heated to 700° in **sulphur** vapour, and chromium sulphide is formed; and when heated to 1200° in a current of **hydrogen sulphide,** crystals of chromium sulphide are formed. W. Guertler and T. Liepus observed no reaction with 48 hrs.' exposure to 10 and 50 per cent. soln. of **sodium sulphide** with or without the addition of alkali-lye. N. Domanicky found that chromium is not readily attacked by an ethereal soln. of **sulphur monochloride;** and E. H. Harvey, that it is not attacked in a year at room temp. J. Férée said that pyrophoric chromium unites with **sulphur dioxide** with incandescence. H. V. Regnault, E. M. Péligot, H. Moissan, W. Hittorf, F. Wöhler, and E. Jäger and G. Krüss noted that chromium is but slowly attacked by dil. **sulphuric acid** in the cold, the action is slow even when hot, hydrogen is given off, and, if the action takes place out of contact with air, blue crystals of chromous sulphate can be obtained from the soln. Boiling, conc. sulphuric acid with chromium gives off sulphur dioxide. W. Guertler and T. Liepus observed no action in 48 hrs. with 10 per cent. $H_2SO_4$ and with 20 per cent. $H_2SO_4$ sat. with sodium sulphate. W. Rohn found that 10 per cent. sulphuric acid dissolves 0·01 grm. per sq. dm. per 24 hrs. in the cold, and 45 grms. per sq. dm. per hr. when hot; and D. F. McFarland and O. E. Harder, that the normal acid dissolves 1·00 mgrm. per sq. in. per week. J. Voisin, and A. Burger studied the action of sulphuric acid on the metal. G. Walpert observed that the rate of dissolution and the electrode potential of

chromium in 4*N*-$H_2SO_4$—unlike the case with iron (*q.v.*)—is raised by the addition of small proportions of potassium or sodium chloride, bromide, and iodide, and the period of induction is shortened. The addition of larger proportions of these salts may act in the reverse way. Gelatin reduces the rate of dissolution of chromium in the acid; additions of acetic acid act similarly. E. Beutel and A. Kutzelnigg studied the films produced by a boiling soln. of **sodium thiosulphate** and lead acetate. M. G. Levi and co-workers found that a soln. of **potassium persulphate** rapidly dissolves chromium as chromic acid, and a little gas is evolved; the process of dissolution is slow with a soln. of **ammonium persulphate**.

A. Binet du Jassonneix, I. Zschukoff, and J. Férée found when pyrophoric chromium unites with **nitrogen,** a bronze-coloured nitride is formed. F. Adcock found that molten chromium rapidly absorbs nitrogen up to the extent of 3·9 per cent., and G. Valensi, and R. Blix also obtained evidence of the formation of a nitride when nitrogen is absorbed by chromium at an elevated temp. E. Martin studied the occlusion of nitrogen and the formation of nitrides by chromium; G. Tammann suggested complexes are formed under these conditions rather than ordinary compounds—*e.g.* $Cr_4(N_2)$, and $Cr_2(N_2)$. G. G. Henderson and J. C. Gallety observed that at 850° **ammonia** reacts with chromium forming the nitride. W. Guertler and T. Liepus observed that no reaction with 10, 50, and 70 per cent. ammonia soln. occurs in 48 hrs.; and D. F. McFarland and O. E. Harder, that a normal soln. dissolves 1·60 mgrms. per sq. in. per week. F. W. Bergstrom found that **potassamide** in liquid ammonia soln. acts very slowly or not at all on chromium. J. Férée, and F. Emich said that at ordinary temp. pyrophoric chromium unites with **nitric oxide** with incandescence forming a mixture of chromium oxide and nitride. E. Müller and H. Barck observed that nitric oxide has no action on chromium at 600°. A. L. Bernoulli said that nitric oxide is absorbed by chromium, and when the metal is treated with **nitric acid,** and thoroughly washed, it liberates a measurable amount of nitric oxide when allowed to remain in water for several hrs.—active chromium does not yield the gas under similar conditions. W. Rohn found that 10 per cent. nitric acid dissolves 0·013 grm. per sq. dm. per 24 hrs. in the cold, and none in an hour when hot; W. Guertler and T. Liepus observed no action in 48 hrs. with 10 and 50 per cent. nitric acid, or with aqua regia; and D. F. McFarland and O. E. Harder found that normal nitric acid dissolves 0·35 mgrm. per sq. in. per week. W. Hittorf said that nitric acid makes chromium passive. F. Wöhler, E. Jäger and G. Krüss, H. St. C. Deville, and C. C. Palit and N. R. Dhar said that dil. or conc. nitric acid does not act on chromium. H. Moissan said that chromium is very slowly attacked by dil. nitric acid; and that fuming nitric acid, as well as aqua regia, have no action on the metal. E. Frémy, and J. J. Berzelius also noted the resistance the metal offers to attack by aqua regia. A. Granger observed that chromium is attacked by **phosphorus** at 900°. W. Hittorf found that **phosphoric acid** makes chromium passive. W. Rohn found that 10 per cent. phosphoric acid dissolves no chromium in 24 hrs. when cold, or in an hour when hot. He also found that 10 per cent. **acetic acid** dissolves 0·13 grm. per sq. dm. per 24 hrs. in the cold, and 0·03 grm. per sq. dm. per hr. when hot.

According to H. Moissan, chromium reacts with **carbon** when strongly heated, forming a carbide; the chromium also undergoes a process of concentration as in the case of iron. The reaction between carbon and chromium was studied by K. Nischk, R. Kraiczek and F. Sauerwald, and E. Tiede and E. Birnbräuer. G. Charpy said that **carbon monoxide** reacts with chromium at 1000°, forming a mixture of carbon and chromic oxide. H. Moissan also found that at 1200° a mixture of carbon monoxide and **carbon dioxide** attacks chromium superficially, and the metal acquires a crust of chromic oxide mixed with carbon. Hence, the impossibility of obtaining chromium free from carbon in an ordinary metallurgical furnace, even when using crucibles or quicklime. Chromium is oxidized when heated in carbon monoxide. S. Medsforth studied the promotor action of chromium on nickel as catalyst in the hydrogenation of carbon monoxide or

dioxide. W. Guertler and T. Liepus observed no action after 4 weeks' exposure to water sat. with carbon dioxide. W. Hittorf said that **citric acid** makes chromium passive ; and a similar result was obtained with **formic, acetic, and tartaric acids.** S. Hakomori studied the action of chromium on ammonia in the presence of tartaric acid and glycerol. J. H. Mathews observed that a soln. of **trichloractic acid** in nitrobenzene does not attack chromium. W. Guertler and T. Liepus observed no reaction with citric and tartaric acids during 24 hrs.' exposure. D. F. McFarland and O. E. Harder observed that fatty acids dissolved 1·23 mgrms. per sq. in. per week ; and C. B. Gates, that chromium is not attacked by **oleic acid** at room temp. J. G. Thompson and co-workers studied the action of soln. of **urea,** and of **ammonium carbonate** on the metal. H. S. Taylor and G. B. Kistiakowsky discussed chromic oxide as a methanol catalyst ; and O. Schmidt as a hydrogenation catalyst. H. Moissan round that when heated in an electric furnace chromium readily unites with **silicon,** forming a silicide ; and with **boron,** forming a boride. E. Vigouroux found that at 1200° chromium reacts with **silicon tetrachloride,** forming a silicide ; and, according to W. Treitschke and G. Tammann, it attacks **porcelain** vigorously at 1600°.

A. Burger said that the vapour of **calcium** has no appreciable action on chromium at a red-heat. W. G. Imhoff found that chromium resists attack by molten **zinc** more readily than does iron or steel. W. Treitschke and G. Tammann found that the action on **magnesia** at 1700° is quite small. H. Moissan said that fused **potassium hydroxide** has no appreciable action on chromium at dull redness ; but J. J. Berzelius said that at a red-heat, in air, the chromium is attacked. W. Guertler and T. Liepus observed no reaction with 10 and 50 per cent. soln. of **sodium hydroxide** during 8 hrs.' exposure. M. Leblanc and O. Weyl found that potassium hydroxide between 550° and 660° has a slight action on chromium, forming traces of potassium and hydrogen. D. F. McFarland and O. E. Harder observed that normal sodium hydroxide dissolves 0·35 mgrm. per sq. in. per week, and normal **sodium chloride,** 2·00 mgrms. per sq. in. per week. U. Sborgi and G. Cappon found that in a soln. of **calcium and ammonium nitrate** in ethyl alcohol, chromium is passive with low current pressures, and with high pressures, chromous ions are formed. J. J. Berzelius, F. Wöhler, and H. Moissan observed that chromium is energetically attacked by fused **potassium nitrate** at a dull red-heat ; and that the attack by fused **potassium chlorate** is even more vigorous—the chromium floats on the chlorate producing vivid incandescence. H. Moissan said that chromium is slowly attacked by **mercuric chloride ;** W. Guertler and T. Liepus observed a slight action with a 1 : 500 soln. at 90° ; and no action with **magnesium chloride** soln.

**Some reactions of analytical interest.**—Chromic salts give no precipitate with **hydrochloric acid ;** and **hydrogen sulphide** gives no precipitate in acidic soln., but in alkaline soln. **ammonium sulphide** precipitates chromic hydroxide ; and a similar precipitate is obtained with **ammonia.** According to F. Jackson,[2] the reaction with ammonia is sensitive to 1 : 4000 ; and with ammonium sulphide to 1 : 8000. The chromic hydroxide is slightly soluble in an excess of ammonia forming a violet soln. The precipitation should be made from a boiling soln. using as little ammonia as possible. Aq. soln. of the **alkali hydroxides** also precipitate chromic hydroxide, and with an excess of the alkali, some chromium passes into soln. : $3KOH+Cr(OH)_3 \rightleftharpoons 3H_2O+Cr(OK)_3$, an excess of water or boiling makes the reaction pass from right to left, and unlike the corresponding case with aluminium, nearly all the chromium is precipitated as hydroxide. **Alkali carbonates** also precipitate chromic hydroxide ; and similarly J. N. von Fuchs found that **calcium carbonate** precipitates a green chromic carbonate ; and H. Demarçay obtained a similar result with **strontium, barium, and magnesium carbonates.** H. Rose said that with cold soln. barium carbonate slowly precipitates green hydrated chromic oxide. A boiling soln. treated with **sodium thiosulphate** gives a precipitate of chromic hydroxide. With **alkali phosphates,** a green precipitate of chromic phosphate

is formed; this is soluble in mineral acids and in cold acetic acid; when the acetic acid soln. is boiled, chromic phosphate is again precipitated. **Alkali acetates** give no precipitate with cold or boiling soln., but if aluminium and ferric salts are present in excess, basic acetate is precipitated; if the chromic salt be in excess, the precipitation is incomplete. **Peroxides**—*e.g.* hydrogen, sodium or lead dioxide—and **per-salts**—*e.g.* persulphates, perborates, and percarbonates—convert alkaline soln. into yellow chromates; similarly, **potassium permanganate** in hot, alkaline soln. converts the chromic salt into a chromate. When chromic oxide or hydroxide is fused with alkalies and other bases, in air, chromate is formed.

A yellow soln. of the chromate becomes orange coloured when treated with dil. **sulphuric acid**; and with conc. sulphuric acid, red needles of chromic acid may be formed, and the soln. may become green with the evolution of oxygen: $2CrO_3+3H_2SO_4=3H_2O+3O+Cr_2(SO_4)_3$. In neutral soln., **silver nitrate** gives a brownish-red precipitate soluble in ammonia and mineral acids; with conc. soln. of potassium dichromate, silver nitrate may precipitate reddish-brown silver dichromate which when boiled with water forms a soln. of chromic acid, and normal silver chromate. With **lead acetate,** lead chromate is precipitated; the precipitation is incomplete with lead nitrate unless the soln. contains acetates. According to P. Harting, a precipitate is obtained with lead salts and potassium dichromate and the reaction is sensitive to 1 : 111,982; T. G. Wormley gave 1 : 107,700; and F. Jackson, to 1 : 32,000. Neutral chromates give yellow barium chromate when treated with **barium chloride**; the precipitate is soluble in mineral acids, and insoluble in acetic acid. If dichromates are used the precipitation is incomplete except in the presence of alkali acetates. According to F. Jackson, the reaction with barium salt and potassium dichromate is sensitive to 1 : 256,000. A cold soln. of a chromate gives brown mercurous chromate when treated with **mercurous nitrate**; and if the soln. is boiled, fiery-red, normal mercurous chromate is formed. **Reducing agents**—*e.g.* hydrogen sulphide, sulphur dioxide, etc.—convert the chromates into green chromic salts. According to P. Cazeneuve,[3] N. M. Stover, and A. Moulin, chromates give a purple, violet, red or brown coloration with **diphenylcarbazide,** or the acetate, in alcoholic soln. According to K. Pander, and J. Froidevaux, **guaiacum tincture** gives an evanescent, blue coloration with chromates. J. Meyerfeld obtained a yellowish-red coloration with an aq. soln. of **pyrogallol dimethyl ether**; and P. N. van Eck obtained a blue coloration with an aq. soln. of **α-naphthylamine** and tartaric acid; D. Lindo, a brown band with **phenol,** and a rainbow band with **orcinol**; P. König obtained a red or violet coloration with **1 : 8 dihydroxynaphthalene-3 : 6-disulphonate**—it is said to be sensitive to 0·0000008 grm. of chromium in 10 c.c. L. C. A. Barreswil found that if an acidic soln. of a chromate be treated with **hydrogen dioxide** and then shaken with ether, the upper ethereal layer will be coloured blue—*vide infra*, perchromates. S. N. Chakrabarty and S. Dutt studied organic syntheses with chromium powder.

**The physiological action of chromium salts.**—According to G. C. Gmelin,[4] chromic chloride is less active than normal potassium chromate; 1·9 grms. of the latter killed a rabbit within 2 hrs., while 3 grms. of the chloride had no action. Subcutaneous injections of 0·2 to 0·4 grm. of potassium chromate were found by E. Gergens, and C. Posner to act with great intensity on rabbits, and death often occurred within a few hours. E. V. Pelikan found that 0·06 to 0·36 grm. of potassium dichromate is fatal to rabbits and dogs. Workmen exposed to the dust of potassium dichromate were stated by B. W. Richardson to acquire a bitter disagreeable taste in the mouth with an increase of saliva which helps to get rid of most of the poison, and little ill-effects are observed. Those who inspire by the nose suffer from inflammation of the septum, which gradually gets thin, then ulcerated, and finally the whole septum is destroyed. The dichromate also causes painful skin eruptions, and ulcerations which the workmen call *chrome holes*. These skin diseases start from an excoriation; so long as the skin remains whole, there is little local effect.

Horses, also, about the works develop ulcerations if the salt get into wounds or cracks in the legs ; and the animals may lose their hoofs. Cases of poisoning by chromates are rare. They have been recorded by J. Maschka, E. O. MacNiven, W. A. McLachlan, J. J. Bloomfield and W. Blum, A. M'Crorie, G. Wilson, J. T. Gadsby, A. D. Walker, G. Leopold, O. von Linstow, and R. C. Smith. The symptoms are severe gastro-intestinal inflammation, accompanied by depression, stupor, and death. The subject was discussed by A. Hébert, H. Becker, L. Lewin, etc. The objectionable uses of chromates for preserving milk, etc., was discussed by G. Denigès,[5] and J. Froidevaux ; the antiseptic action of chromates by A. Müller, P. Miquel, C. Chamberland and E. Roux, P. J. Laujorrois, J. F. Clark, C. H. Pander, A. Strubell, H. Schulz, H. Coupin, etc. M. E. Pozzi-Escot found that chromic salts are less poisonous than potassium chromate and dichromate, chrome-alum or chromic acid towards the lower fungi—*e.g. saccharomycetes.* P. König found that with certain minute concentrations plant life may be stimulated by chromium salts and chromates ; the toxic action is greater the higher the degree of oxidation of the chromium. A wheat plant was killed by a 0·0064 per cent. soln. of sodium dichromate, and a 0·5 per cent. soln. of chrome-alum was needed to produce a similar result. T. Pfeiffer and co-workers could not find any beneficial stimulating effect of chromite, or of potassium dichromate on the growth of oats and barley.

**Some uses of chromium.**—One of the most important applications of chromium is in the production of various alloys,[6] principally ferrochromium alloys for the manufacture of special steels many of which contain about 2 per cent. of chromium and a small proportion of other metals—*vide* the alloys of iron. The chrome-alloy steels are hard and tough. They are used in making armour-plate. armour-piercing projectiles, burglar-proof safes ; tyres, axles, springs for railways and motor-cars, stamp-mill shoes, crusher jaws, the so-called rustless cutlery, *stellite*—an alloy containing chromium, cobalt, and molybdenum and tungsten—for high speed tools which retain their cutting edge at temp. approaching redness ; *nichrome*—nickel, chromium, iron (60 : 14 : 15), a high temp. resistance alloy ; chromium-vanadium steel ; chromium magnet steel ; heat-resisting and acid-resisting steels ; etc. Chromium plating as a protective coating for steel is much employed [7]—*vide supra*, the electrodeposition of chromium. Perhaps the largest demand for chromium is in the form of chromite used as a refractory in certain parts of open-hearth and other furnaces.[8] Chromium compounds are used in tanning certain leathers—chrome leathers ; as a mordant for dyeing ; it is used for impregnating wood, paper, etc., with chromic hydroxide ; and in the preparation of filaments for incandescent lamps. Chromates are used for making gelatine insoluble—for a mixture of gelatine and potassium dichromate becomes insoluble when exposed to light—in colour printing, block printing, heliography, photolithography, photozincography, etc. Chromium compounds are used in making safety matches ; as antiseptics ; in bleaching oils ; in the purification of wood vinegar ; as a component of certain galvanic cells ; an oxidation agent in the preparation of some aniline dyes and in a number of analytical and chemical processes ; as a catalytic agent in the preparation of sulphur trioxide (*q.v.*), and, according to H. W. Underwood,[9] in the hydrogenation of organic compounds.

Chromic oxide is employed as green pigments for paints—chrome-green, emerald-green, Cassal's green, etc.—and it may be associated with other substances—*e.g.* boric oxide, phosphoric oxide, zinc oxide, etc. to produce special tints, there are yellow chromates of lead, etc.—*e.g.* chrome yellow, lemon yellow, Paris yellow, royal yellow, etc. ; red basic lead chromates—*e.g.* chrome-orange, chrome-vermilion, etc. ; and brown, manganese chromate.[10] Chromic oxide is employed in producing on-, in-, and underglaze green colours in enamel, pottery and glass manufacture ; on-glaze yellows employed for on-glaze work, and in enamelling are derived from lead chromate, the on-glaze reds and orange colours, from basic lead chromate. A crimson or pink colour for pottery decoration is based on the result of calcining

stannic oxide with one or two per cent. of chromic oxide; for the coloration of alumina with chromium to form artificial rubies—*vide* alumina. C. J. Smithells [11] described the manufacture of articles from chromium.

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## § 6. The Atomic Weight and Valency of Chromium

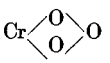
In 1818, J. J. Berzelius [1] represented chromic anhydride by the formula $CrO_6$ but later gave $CrO_3$, and the corresponding formula for chromic oxide became $Cr_2O_3$ by analogy with the sesquioxides of aluminium, iron and manganese. This made the at. wt. of chromium approximate to 52, and is in agreement with the tervalency of chromium in this oxide, and also with the sp. ht. rule ; with the isomorphism of the chromous and ferrous salts observed by C. Laurent ; the isomorphic replacement of chromic, ferric, and aluminium hydroxides in the silicate minerals, spinels and chromites, alums, and complex cyanides ; and the isomorphism of chromates and sulphates—*vide supra*. The at. wt. 52 also agrees with the electrolysis of chromium salts which is in accord with Faraday's law ; with the recognized position of chromium in the periodic table ; and with the frequency of the X-rays observed by H. G. J. Moseley, and M. Siegbahn and W. Stenström.

Chromium under different conditions may act as a bi-, ter-, and sexi-valent element. F. Pintus discussed the possibility of the formation of compounds with *univalent* chromium in such reactions as : $4CrCl_2+4C_6H_5MgBr=(C_6H_5)_4CrCl+3CrCl\ 2MgCl_2+2MgBr_2$. *Bivalent* chromium in the dichloride has a vap. density at 1600° half as much again too high for the simple molecule $CrCl_2$, and, according to L. F. Nilson and O. Pettersson, the chromium is really tervalent $Cr_2{=}Cr{-}Cr{=}Cl_2$ ; but it may be

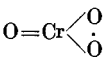
$$Cr<\begin{matrix}Cl{=}Cl\\Cl{=}Cl\end{matrix}>Cr$$

The isomorphism between $CrSO_4.7H_2O$, and $FeSO_4.7H_2O$, indicated by C. Laurent, shows that the bivalency of chromous chromium corresponds with the bivalency

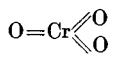
of ferrous iron. The *tervalency* of chromium has been more definitely established by L. F. Nilson and O. Pettersson's observations on the vap. density of chromic chloride; F. Hein and E. Markert's observations on triphenyl chromium, $Cr(C_6H_5)_3$; and G. Urbain and A. Debierne's observations on the vap. density of chromic acetylacetonate. There is also the isomorphism of chromium with tervalent aluminium in the alums. W. Just, W. Eissner, E. Markert, and F. Hein and co-workers also prepared tetraphenyl chromium, $Cr(C_6H_5)_4$, in which the metal is presumably *quadrivalent*; and possibly *quinquevalent* in the compounds of the type $Cr(C_6H_5)_4OH$. The *sexivalency* of chromium is indicated by F. Hein's observations on the vap. density of chromyl chloride; and by the relations between sulphur trioxide, $SO_3$, and chromic trioxide, $CrO_3$, as illustrated by the isomorphism of the sulphates and chromates observed by E. Mitscherlich, F. Mylius and R. Funk, and H. Salkowsky. Of course, chromium, in chromic anhydride, may be bi- or quadri-valent



Bivalent.



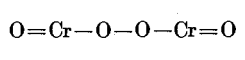
Quadrivalent.



Sexivalent.

and W. Manchot believed that the chromium is quadri- not sexi-valent, and similarly also with the other cases of sexivalent chromium; hence, the whole force of the argument turns on the analogy with what he assumed to be sexivalent sulphur. W. Manchot and R. Kraus reported chromium dioxide, $CrO_2$, in which the chromium is bi-, ter-, or quadrivalent

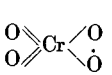
Bivalent.



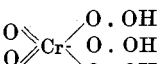
Tervalent.

Quadrivalent.

and W. Manchot believed it to be *quadrivalent*. The isomorphism of the complex salts of chromium oxytrichloride, $CrOCl_3$, say $CrOCl_3.2CsCl$ with $CbOCl_3.2CsCl$, observed by R. F. Weinland and co-workers, agrees with the assumption that chromium is here quinquevalent. F. Olsson obtained addition products of quinquevalent chromium. R. Luther and T. F. Rutter also assumed that in the reaction between hydriodic acid and chromic acid, the chromium is first reduced to a quinquevalent stage and then to a quadrivalent stage. According to E. H. Riesenfeld, chromium in chromium tetroxide, $CrO_4$, is sexivalent, and in the perchromate $H_3CrO_8$, *septivalent*:



$CrO_4$



$H_3CrO_6$

A. Werner,[2] and P. Pfeiffer and co-workers described optically active chromic diaquodiethylenediamine salts, $[Cren_2(H_2O)_2]X_3$; chromic hydroxyaquodiethylenediamine salts, $[Cren_2(OH)(H_2O)]X_2$; A. Werner, and P. Pfeiffer and co-workers, chromic dichlorodiethylenediamine salts, $[Cren_2Cl_2]X$; chromic dibromodiethylenediamine salts, $[Cren_2Br_2]X$; and chromic dithiocyanatodiethylenediamine salts, $[Cren_2(SCy)_2]X$.

J. J. Berzelius [3] made the first serious determination of the at. wt. of chromium; he precipitated lead nitrate with an alkali chromate, and weighed the resulting lead chromate. His results for the at. wt. gave 56 from the ratio $Pb(NO_3)_2 : PbCrO_4$; and 54 from $BaCrO_4 : BaSO_4$. Later observers have shown that the method is unreliable—with conc. soln., the precipitate adsorbs alkaline salts, and with dil. soln., the precipitation is incomplete. E. M. Péligot analyzed chromous acetate and chromium chloride, and obtained a value for the at. wt. 52·5, much lower than that of J. J. Berzelius; and V. A. Jacquelain obtained a very low result, 50·1. In neither case were sufficient data described in the reports to enable estimates to be

made of the value of the work. Some general observations on the subject were made by W. A. Noyes, and S. Lupton.

In 1846, N. J. Berlin obtained 52·6 to 52·9 from the ratio $2AgCl : Ag_2CrO_4$; 52·3 to 52·5 from $Cr_2O_3 : 2Ag_2CrO_4$; 52·6 from $2AgCl : Ag_2Cr_2O_7$; 52·3 from $Cr_2O_3 : Ag_2Cr_2O_7$; and 52·0 from $Pb(NO_3)_2 : PbCrO_4$. A. Moberg obtained 53·2 from the ratio $Cr_2O_3 : Cr_2(SO_4)_3$; 53·7 from $Cr_2O_3 : Cr_2(SO_4)_3$; and 53·6 from $Cr_2O_3$ : chrome-alum. J. Lefort calculated 53·1 from the ratio $BaCrO_4 : BaSO_4$; and R. Wildenstein, 53·6 from $BaCrO_4 : BaCl_2$. F. Kessler obtained 52·2 to 52·4 from the ratio $KClO_3 : K_2Cr_2O_7$; M. Siewert, 52·05, from $CrCl_3 : 3AgCl$; 52·1, from $Ag_2Cr_2O_7 : 2AgCl$; and 52·0, from $Ag_2Cr_2O_7 : Cr_2O_3$; H. Baubigny, 52·1 from $Cr_2(SO_4)_3 : Cr_2O_3$; S. G. Rawson, 52·2 from $(NH_4)_2Cr_2O_7 : Cr_2O_3$; F. W. Meinecke, 52·2, from $(NH_4)_2Cr_2O_7 : Cr_2O_3$; 52·08, from $4AgCl : Cr_2O_3$; 52·06, from $Ag_2CrO_4 : I_2$; 52·2, from $[Ag_2(NH_3)_4]CrO_4 : I_2$; 52·10, from $K_2Cr_2O_7 : KClO_3$; and 52·13, from $(NH_4)_2Cr_2O_7 : I_2$; F. G. Nunez, 52·025, from $CrCl_2O_2 : 2AgCl$; G. P. Baxter, E. Mueller and M. A. Hines. 52·005, from $2AgCl : Ag_2CrO_4$, and 52·012, from $2AgBr : Ag_2CrO_4$; and G. P. Baxter and R. H. Jesse, 52·016, from $2AgBr : Ag_2Cr_2O_7$. J. Meyer gave $52·01 \pm 0·01$ as the best representative value; F. W. Clarke, $52·0193 \pm 0·0013$; while the International Table for 1926 gave 52·01.

The **atomic number** of chromium is 24. F. W. Aston [4] found chromium has four **isotopes** with mass numbers and percentage abundance respectively 50 and 4·9; 52 and 81·6; 53 and 10·4; and 54 and 3·1, making the at. wt. 52·011. N. Bohr gave for the **electronic structure** (2) for the K-shell; (4, 4) for the L-shell; (4, 4, 4) for the M-shell; and (2) for the N-shell. Speculations on the subject were made by S. Meyer, R. H. Ghosh, H. Lessheim and co-workers, C. D. Niven, K. Höjendahl, R. G. W. Norrish, R. Samuel and E. Markowicz, D. M. Bose, F. Hund, I. Tamm, R. Ladenburg, A. S. Russell, P. Ray, J. D. M. Smith, J. N. Frers, O. Feussner, C. G. Bedreag, A. Sommerfeld, and N. Collins. Evidence of **atomic disintegration** by bombardment with $\alpha$-rays was observed by H. Pettersson and G. Kirsch. The subject was discussed by G. I. Podrowsky.

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## § 7. The Alloys of Chromium. Chromides

G. Hindrichs [1] prepared **copper-chromium alloys** by the direct union of the elements. G. Hindrichs said that in the molten state the elements are only slightly soluble in one another; H. Moissan said that molten copper can take up 0·5 per cent. of chromium; and A. B. du Jassonneix that boiling copper can take up 1·6 per cent. of chromium. G. Hindrichs found that the emulsion formed by the two elements does not separate readily into two layers. E. Siedschlag's f.p. curve is shown in Fig. 7. E. Siedschlag found that there is only a partial miscibility in the liquid state with a eutectic at 1076° and 1·5 per cent. of copper. The limits within which a mixture of the two liquids is formed are 37 and 93 per cent. of chromium, above 1470°. Only heterogeneous mixtures of two kinds of crystals are obtained in the solid state, chromium, and a eutectic rich in copper. E. Placet, the Electrometallurgical Co., and D. S. Ashbrook deposited electrolytically a mixture of the two elements. The Neo-Métallurgie Marbeau, and L. P. Hamilton and E. F. Smith heated a mixture of chromium and copper oxides with carbon; P. L. Hulin reduced the mixed oxides with sodium; and H. Goldschmidt, with aluminium. G. Hindrichs reduced a mixture of chromic oxide, potassium dichromate, and cupric sulphide. H. Goldschmidt said that an alloy with 10 per cent. of chromium is greyish-red and harder than copper. L. P. Hamilton and E. F. Smith prepared a greyish-red alloy with 7 per cent. chromium and a sp. gr. 8·346. The Electrometallurgical Co. reported that chromium containing one-thousandth part of copper is harder and tougher than copper; alloys with 0·5 to 20 per cent. of chromium have approximately the toughness of steel, and they are very resistant towards acids, and alkalies, and they also resist high temp. M. G. Corson studied the hardness of the alloys. D. F. McFarland and O. E. Harder observed that the sp. gr. of the alloys with 91·68, 83·02, and 74·05 per cent. of copper were respectively 8·78, 8·60, and 8·47; and Brinell's hardness, respectively <68, 69, and 68. The corrosion of the alloys by normal hydrochloric, sulphuric, and nitric acids, normal soln. of sodium chloride, and hydroxide, ammonium hydroxide and

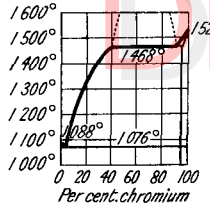


FIG. 7.—Freezing-point Curve of Cu–Cr Alloys.

DropBooks

fatty acids, expressed in terms of the loss in mgrms. per sq. in. per week, are indicated in Table II.

TABLE II.—THE CORROSION OF CHROMIUM-COPPER ALLOYS.

| Copper (Per cent.). | NaOH. | HCl. | $H_2SO_4$. | $HNO_3$. | NaOH. | $NH_4OH$. | Fatty acids. |
|---|---|---|---|---|---|---|---|
| 91·68 | 4·33 | 42·8 | 17·20 | 12·60 | 10·40 | 41·80 | 10·50 |
| 83·02 | 4·00 | 38·3 | 14·20 | 13·10 | 9·6 | 57·50 | — |
| 74·05 | 4·60 | 30·3 | 16·40 | 60·30 | 8·86 | 67·50 | 10·70 |

The **silver-chromium alloys** have not been closely studied. According to G. Hindrichs, liquid chromium and silver are only partially miscible; solid soln. are not formed. The addition of 5 per cent. of silver lowers the f.p. of chromium 50°. A reconstructed curve by G. Hindrichs is shown in Fig. 8. L. Jordan and co-workers measured the hardness, tensile strength, and elongation of these alloys. R. Vogel and E. Trilling's observations on the **gold-chromium alloys** are summarized in Fig. 9. No compounds of definite composition are formed. There are three kinds of mixed crystals, one rich in chromium, and two rich in gold. The Greek letters in Fig. 9 refer to the solid soln.

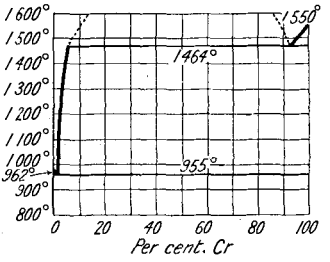


FIG. 8.—Freezing-point Curve of Ag–Cr Alloys.

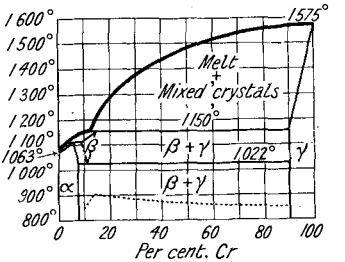


FIG. 9.—Freezing-point Curve of Au–Cr Alloys.

According to H. le Chatelier,[2] a **zinc-chromium alloy,** with 7 per cent. Cr, can be obtained by melting zinc mixed with alkali and chromic chloride. G. Hindrichs found that molten zinc dissolves a little chromium; an alloy with 5 per cent. of chromium had a break 10°–15° above the m.p., and an arrest near the m.p. of zinc. No **cadmium-chromium alloy** could be obtained by heating a mixture of the two elements for 6 hrs. at 650°.

A. S. Russell and co-workers [3] found chromium to be slightly soluble in mercury. G. Tammann and J. Hinnüber said that the solubility of chromium in mercury is $3{\cdot}1\times10^{-11}$ per cent. C. F. Schönbein, N. Bunge, Z. Roussin, and C. W. Vincent prepared a **mercury-chromium alloy** or **chromium amalgam,** by the action of potassium or sodium amalgam on a conc. soln. of chromic chloride; and H. Moissan obtained the amalgam by a similar process, as well as by the action of sodium amalgam on chromous chloride, bromide, or iodide. R. Myers obtained it by the electrolysis of a soln. of chromic sulphate in dil. sulphuric acid using a platinum anode, and mercury cathode; J. Férée found that with a soln. of chromic chloride the yield is poor. H. Moissan said that the amalgam is less fluid than mercury; and J. Férée, that it decomposes in air into chromous oxide and mercury. G. Tammann and J. Hinnüber obtained amalgams by reducing soln. of chromium sulphate with a mercury cathode. H. Moissan added that in air, the amalgam acquires a black film of oxide. It is slowly decomposed by dry air, and rapidly in moist air. R. Myers also found that it is rapidly decomposed by water. C. F. Schönbein observed that when the amalgam is shaken with water and air some hydrogen

dioxide is formed; this reaction is favoured by dil. sulphuric acid. H. Moissan found that the amalgam is insoluble in boiling, conc. sulphuric acid, and that it is soluble in dil. sulphuric acid. It is soluble in nitric acid, and T. Dieckmann and O. Hauf added that with dil. nitric acid the amalgam forms chromous oxide and mercury. A. S. Russell and co-workers found that the order of removal of metals from mercury amalgam by an oxidizing agent is: Zn, Cd, Mn, Tl, Sn, Pb, Cu, Cr, Fe, Bi, Co, and Ni. According to J. Férée, only dil. amalgams are produced by the action of sodium amalgams on chromic chloride, or by the electrolysis of chromium salts with a mercury cathode; better results are obtained by electrolyzing a soln. containing 160 grms. of chromic chloride and 100 grms. of conc. hydrochloric acid in 740 grms. of water by means of a powerful current with a mercury cathode and a platinum anode. Using a current of 22 ampères and a mercury surface of 8·05 sq. cm. he obtained 1·5 kilo. of a solid chromium amalgam. When dried and filtered through chamois leather, the amalgam has the composition **mercury tritachromide,** $Hg_3Cr$. When this is subjected to a press. of 200 kgrms. per sq. cm., it loses mercury and yields **mercury monochromide,** HgCr. The first amalgam is soft, brilliant, and alters but little in air, but when heated loses mercury without melting and oxidizes rapidly; the second is brilliant and harder, but alters more readily. When distilled in vacuo below 300°, they both yield chromium which is pyrophoric at ordinary temp. M. Rabinovich and P. B. Zywotinsky observed that chromium can be dispersed in mercury above the solubility limit and so form a colloidal soln.

F. T. Sisco and M. R. Whitmore [4] obtained **aluminium-chromium alloys** with up to 5 per cent. aluminium, by direct fusion of the two elements. G. Hindrichs could not obtain alloys with more than 70 per cent. chromium by heating a mixture of the two elements in an electric furnace. The alloys were obtained by H. Moissan by reducing chromic oxide with aluminium in excess. G. Hindrichs said that the best mode of preparing the alloys is by igniting a mixture of aluminium, chromic oxide, and potassium dichromate. C. Combes obtained crystalline alloys by the action of the vapour of chromic chloride on aluminium; F. Wöhler obtained the alloys by fusing a mixture of aluminium with twice its weight of violet potassium chromic chloride, $KCrCl_4$, or of a 1 : 2 mixture of potassium and chromic chlorides; and extracting the cold mass first with water, and then with dil. alkali-lye to remove free aluminium. G. Hindrichs found that mixtures with between 5 and 55 per cent. of chromium form two liquid layers, Fig. 10, and there is evidence of the formation of **aluminium trichromide,** $AlCr_3$, whose m.p. lies above 1600°. L. Guillet obtained alloys corresponding with *aluminium chromide,* AlCr, and *aluminium tetrachromide,* $AlCr_4$, in the form of silver-grey powders of the respective sp. gr. 4·93 and 6·75 at 20°. H. Schirmeister, J. W. Richards, and E. S. Sperry made some observations on these alloys. F. Wöhler regarded his product as the monochromide, and he described it as forming tin-white, tetragonal plates, or rectangular tetragonal prisms resembling idocrase. It melts at a higher temp. than nickel, forming, when cold, a hard, brittle mass of sp. gr. 4·9. When heated in air, it acquires a steel-coloured lustre without oxidizing further; when heated in hydrogen chloride, some silicon chloride is formed from the impurities present, chromous and aluminium chlorides are also produced; hydrochloric acid attacks the alloy with the evolution of hydrogen; warm, conc. sulphuric acid develops hydrogen with the separation of sulphur; and it is not attacked by conc. nitric acid, or alkali-lye.

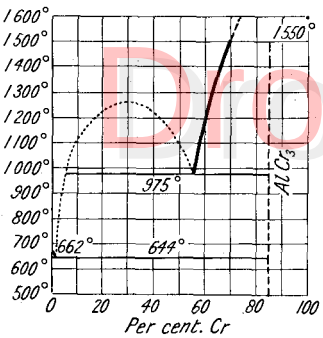


FIG. 10.—Freezing-point Curve of Al–Cr Alloys.

According to G. Hindrichs,[5] **tin-chromium alloys** are produced within a very

narrow range ; the f.p. of chromium is lowered by the addition of up to 10 per cent. of tin ; and mixed crystals are formed up to 6 per cent. of tin—*vide* Fig. 11 ; beyond this, two liquid phases are formed one of which is pure tin. N. A. Puschin said that alloys are soft until about 90 at. per cent. Cr. is present, when they are hard

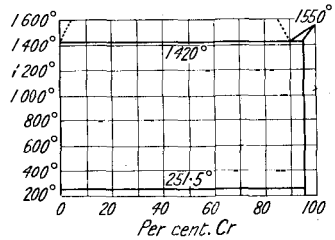


FIG. 11.—Freezing-point Curve of Sn–Cr Alloys.

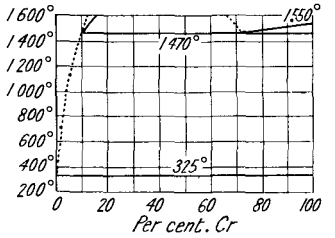


FIG. 12.—Freezing-point Curve of Pb–Cr Alloys.

and brittle ; the e.m.f. curve of the cell Sn | *N*-KOH | $SnCr_n$ shows no sign of either chemical combination or of solid soln. With *n* per cent. Cr, the potentials, *E* in millivolts, are :

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *n* . | 20 | 25 | 33 | 50 | 67 | 75 | 90 | 95·8 | 100 |
| *E* . | −16 | −2 | −1 | −1 | −4 | −3 | −4 | 10 | 302 |

G. Hindrichs said that **lead-chromium alloys** can be formed by melting a mixture of the two elements above 1600°. Much lead is volatilized. The addition of 27 per cent. of lead lowers the f.p. of chromium 80°—*vide* Fig. 12 ; alloys with more than this proportion of lead separate into two layers one of which is lead alone, W. von Bolton obtained alloys with **tantalum and chromium**.

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## § 8. The Lower Chromium Oxides

The metals of the chromium family can produce an extraordinary number of compounds ;[1] they can behave as 2-, 3-, 4-, 5-, 6-, and in some cases as 8-valent elements. Hence, one element can form nearly all the types of compounds which characterize the individual elements. The lower oxides have basic properties, while the higher oxides are markedly acidic ; the intermediate oxides—like those of molybdenum, tungsten, and uranium dioxides—are indifferent oxides and resemble in some respects the peroxides of lead and manganese. The lowest oxide of chromium is a strong reducing agent, while the acidic oxide acts as a strong oxidizing agent. All these elements readily form oxides with a composition intermediate between two simpler oxides, and which appear to be salt-like compounds in which the higher oxide plays the rôle of acid, and the lower oxide, base. The intermediate oxides of chromium are not analogous with those of uranium—in the first case the intermediate oxide appears as a compound of the sesqui- and tri-oxides ; and in the other case, a compound of the di- and tri-oxides. The existence of the dioxide of chromium is not so unequivocally established as the dioxides of molybdenum, tungsten, and uranium ; and the peroxide behaves as if it were a compound of the tri- and sesqui-oxide. Three members of the group—molybdenum, tungsten, and uranium—are closely analogous in the nature of the oxides formed, but chromium differs in many ways from the others—*e.g.* in the unstability of chromic trioxide, and the formation of no chloride higher than $CrCl_3$.

A. Moberg[2] obtained **chromium monoxide,** or **chromous oxide,** CrO, by the action of hydrogen or the vapour of alcohol on red-hot chromic oxide, and by heating chromous chloride with sodium carbonate or calcium oxide. It was also similarly obtained by L. Clouet, and E. M. Péligot. J. Férée obtained the oxide by the decomposition of chromium-amalgam in air. T. Dieckmann and O. Hauf said that the oxide is most conveniently made by the action of dil. nitric acid on chromium amalgam ; the mercury passes into soln., chromous oxide remains as a black powder. Hydrogen at 1000° reduces chromous oxide to the metal. According to J. Férée, when the black powder is triturated in a mortar, it oxidizes and glows, forming chromic oxide, and likewise also when heated in air. It is insoluble in dil. nitric or sulphuric acid, and it reacts with hydrochloric acid forming a blue soln., and giving off hydrogen. Carbon dioxide at 1000° converts it into a mixture of chromic oxide and carbide. The constancy of the analytical data by J. Férée favours the assumption that it is not a mixture of chromium and chromic oxide.

If air-free aq. soln. of chromous chloride be treated with an air-free soln. of potassium hydroxide, A. Moberg found that a yellow precipitate of **chromous hydroxide,** $Cr(OH)_2$, is formed. It should be washed with air-free water in an atm. of hydrogen, or carbon dioxide, and dried over sulphuric acid. It is then dark brown. It is stable in dry air, but decomposes when heated : $2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2$ ; it dissolves slowly in conc. acids when freshly precipitated and dried ; but very little dissolves in dil. acids ; and very little in boiling aqua regia. The soln. are green, and contain tervalent chromium because, said A. Moberg, chromium separates as the hydroxide dissolves. F. Allison and E. J. Murphy studied the magneto-optic properties.

The salts of this base, **chromous salts,** are obtained by reducing chromic salts—*vide infra,* chromous sulphate or chloride. The aq. soln. are red, blue, or yellow. The chromous salts readily decompose in the presence of water, forming chromic salts and hydrogen ; and hydrogen is evolved when the aq. soln. are boiled or treated with platinized platinum. R. Peters said that hydrogen is liberated in the oxidation because a chromous salt soln. has a higher potential than hydrogen when in acidic soln. The reaction was studied by R. Stahn. No hydrogen dioxide was observed by W. Manchot and J. Herzog to be formed during the oxidation of chromous salts by atm. oxygen ; and the amount of oxygen absorbed is simply that required for the

oxidation. Hence it is inferred that the oxidation proceeds directly. According to W. Manchot and O. Wilhelms, the primary oxide formed in the oxidation of these salts is a peroxide, say $CrO_2$, because in the presence of an acceptor—say alcohol, or potassium arsenite—which is simultaneously oxidized, two eq. of oxygen are absorbed for each eq. of chromous oxide. J. Piccard found that in the autoxidation of neutral or acidic soln. of chromous salts, chromic acid and chromic salts are formed. Intermediate products, stable for a measurable period, are formed—*vide infra*, chromous chloride. There is first, the easily decomposed hypothetical oxide, represented by $(HO)_2Cr.O.O.Cr(OH)_2$, which acts on potassium iodide in almost neutral soln. It decomposes into the labile oxide $CrO(OH)_2$ by a unimolecular reaction. This oxide in the absence of potassium iodide forms chromic acid, but in the presence of potassium iodide, it is reduced more rapidly than it can form chromic acid. The next oxide, $(HO)_2Cr<\overset{O}{\underset{O}{\cdot}}$, is reduced by potassium iodide in weakly acidic soln. within two minutes. W. Traube and W. Lange found that with chromous hydroxide, oxalic, hydrocyanic, and thiocyanic acids are converted into glycollic acid, methylamine, and hydrogen sulphide, respectively. Azides and azoimide instantaneously yield nitrogen and ammonia. Chloroacetic acid is converted into acetic acid, whilst benzaldehyde yields benzyl alcohol—*vide infra*, chromous chloride.

R. Bunsen [3] reported an oxide $2CrO.Cr_2O_3$, or $3CrO.Cr_2O_3$, to be formed in the electrolysis of soln. of chromic salts—*vide supra*, the electrolytic preparation of chromium. The black, amorphous powder glows when heated in air forming green chromic oxide; it is insoluble in acids. A. Geuther could not prepare an oxide of this composition; and J. Férée obtained a black powder with similar properties, but with the composition $Cr_2O_3.H_2O$, in his study of the electrolysis of soln. of chromic chloride.

According to E. M. Péligot,[4] when an air-free aq. soln. of chromous chloride is treated with air-free alkali-lye in an inert atm., the brown precipitate which is formed gradually in the cold, rapidly when boiled, decomposes, hydrogen is evolved, and a reddish-brown hydrate of **chromosic oxide**, or **chromium tritatetraoxide**, $Cr_3O_4$, or $CrO.Cr_2O_3$, is formed. This can be washed with boiling water, and dried in vacuo. According to A. Moberg, and G. Baugé, it is a *trihydrate*, whereas E. M. Péligot said that it is a *monohydrate*. G. Baugé could not make the monohydrate, but he obtained the trihydrate, $Cr_3O_4.3H_2O$, by treating chromous carbonate with alkali carbonate in boiling water while protected from air. The brown powder loses water when heated, and it suffers autoxidation: $2Cr_3O_4+2H_2O=3Cr_2O_3+H_2+H_2O$. According to G. Baugé, when dried in vacuo at 100°, the yellowish-brown powder has a sp. gr. 3·49. It is converted into chromic oxide by the action at 250° of water-vapour, hydrogen chloride, or an inert gas, hydrogen being evolved; it is also decomposed by chlorine at a dull red-heat, giving chromyl chloride, water, and hydrogen chloride. Although stable in dry air at the ordinary temp., it is rapidly oxidized to chromic oxide in presence of water or when heated; by hydrogen sulphide, it is converted at a somewhat elevated temp. into a crystalline sulphide, whilst it rapidly reduces dil. sulphuric acid at 40°, hydrogen sulphide being evolved if a large quantity of the oxide is employed. When the latter is dissolved in conc. hydrochloric acid, a mixture of chromous and chromic chlorides is formed.

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## § 9. Chromic Oxide

Chromium oxidizes when heated in air to form **chromium hemitrioxide, chromium sesquioxide,** or **chromic oxide,** $Cr_2O_3$; chromic oxide is also produced by calcining the hydroxide—*vide supra*, the extraction of chromium. The analysis of J. J. Berzelius [1] corresponds with this formula; and it is usually supposed to be constituted O=Cr—O—Cr=O; although A. T. Cameron assumed the formula to be Cr≡$O_3$≡Cr. L. N. Vauquelin, H. Moser, J. Persoz, and J. B. Trommsdorff obtained this oxide by heating mercuric chromate; it has a fine green colour if calcined out of contact with air, but it has a brown colour when heated while exposed to air. A. Maus obtained it by heating ammonium chromate; A. A. Hayes, ammonium dichromate: $(NH_4)_2Cr_2O_7=4H_2O+N_2+Cr_2O_3$; J. L. Lassaigne, and H. Moser, a mixture of potassium chromate and sulphur, and extracting the soluble products with water; G. C. Wittstein, H. C. Roth, and E. Dieterich, a mixture of potassium dichromate and sulphur; F. Wöhler, a mixture of potassium dichromate, ammonium chloride, and sodium carbonate; R. T. M. y Luna, G. B. Frankforter and co-workers, a mixture of potassium dichromate and ammonium chloride; and A. L. D. d'Arian, alkali chromate and ammonium sulphate. According to V. H. Roehrich and E. V. Manuel, the reaction between ammonium chloride and potassium dichromate, usually symbolized by R. T. M. y Luna's equation $2NH_4Cl+K_2Cr_2O_7=Cr_2O_3+2KCl+4H_2O+N_2$, varies with the temp. at which the mixture is heated and the relative proportions of the constituents of the mixture. The first visible sign of change occurs at 210° when the mixture becomes yellowish-brown owing to the formation of a chromium dioxide; at 260°, a slate-coloured residue is obtained which when lixiviated with water gives greenish-black crystals of a hydrated chromic oxide. At 370°, with an excess of ammonium chloride, chromium chloride and ammonia are formed; with the potassium dichromate in excess a black residue mixed with unchanged dichromate is formed. Under different conditions chlorine, nitric oxide, nitrogen peroxide and chromium nitride may be formed as by-products. C. H. Binder obtained chromic oxide by heating a mixture of potassium dichromate and starch; C. H. Humphries, from a mixture of chromium trioxide and barium hydroxide. R. Böttger inflamed a mixture of picric acid, potassium dichromate, and ammonium chloride; H. Schöffer inflamed a mixture of sodium dichromate and glycerol; W. Carpmael heated an aq. soln. of an alkali chromate and an organic reducing agent—sugar, sawdust, etc.—above 110°, under press.; and E. A. G. Street obtained it as a product in the electrolysis of a soln. of an alkali chromate with a mercury cathode. F. Wöhler, and J. F. Persoz found that the crystalline oxide is formed when chromyl chloride is decomposed by heat; W. P. Evans, when chromyl fluoride is heated; E. Frémy, when heated potassium chromate is decomposed by chlorine; W. Müller, when potassium chromate at a red-heat is decomposed by hydrogen chloride; V. Kletzinsky, when potassium chlorochromate is melted; J. C. Gentele, when potassium dichromate is decomposed at a high temp.; R. Otto, when potassium dichromate is decomposed by hydrogen at an elevated temp.; A. Ditte, and H. Schiff, when potassium dichromate is decomposed by fusion with sodium chloride; and M. Prud'homme, when potassium dichromate is heated with tin. Crystals of chromic oxide are often produced as a kind of sublimate when mixtures containing chromic oxide are heated in closed vessels in pottery ovens. E. Wydler, and G. F. C. Frick also described the prepara-

tion of the oxide; and W. P. Blake and W. H. Miller observed its formation as a furnace product. C. Ullgren obtained crystals of the oxide by decomposing potassium dichromate mixed with oil, or ammonium chloride and then raising the temp. to a white-heat. V. Kohlschutter and J. L. Tüscher obtained highly dispersed or an **aerosol of chromic oxide** by vaporizing the oxide into a chamber where it is suddenly chilled.

**The physical properties of chromic oxide.**—The **colour** of amorphous chromic oxide is bright green if it has been calcined in a reducing atm., and it may acquire a brown tinge in an oxidizing atm. The tint of commercial oxides varies from brownish-green, to greyish-green, to olive-green to bright grass-green. This may be due to partial crystallization; to the grain-size of the powder; and to the presence of traces of impurity as a result of which the colour of a chromate may be superposed on that of the chrome-green. The amorphous chromic oxide obtained from ammonium dichromate is a voluminous, tea-green powder. A very thin sublimate of chromic oxide is red, and this probably explains the colour of the chrome-tin pink, **1**. 46, 33; and of the ruby, **5**. 33, 10. R. Klemm found a relationship between the proportion of chromium in spinel, corundum, spodumene, beryl, chrysoberyl, topaz, and zircon and the depth of colour. In all but zircon, chromium replaces aluminium, and in zircon, it may replace silicon or zirconium. Small quantities of vanadium may take the place of chromium. Black chromic oxide, insoluble in acids, was obtained by L. Godefroy by heating the hydrate, $Cr_2O_3.3H_2O$; and by E. A. Werner, by heating the succinate. According to O. Hauser, the play of colours of the variety of chrysoberyl called *alexandrite* is produced by a small trace of chromic oxide. I have evidence that the colour of chrome-tin pink or crimson—produced by a trace of chromic oxide on stannic oxide as mordant—probably represents the colour of the highly dispersed chromic oxide. The colour can be produced by depositing the vapour of chromic oxide on stannic oxide or on alumina. According to A. Duboin and others, the colour of the ruby is due to the presence of chromic oxide—**5**. 33, 10. The red colour of the so-called chrome-tin crimson is thus equivalent to the crimson and purple colour of the purple of cassius where colloidal gold is dispersed on the same mordant; and also equivalent to the copper red—*rouge flambé*—where presumably colloidal copper is deposited on the same mordant. The chrome-tin crimson has been discussed by H. A. Seger, F. Rhead, A. S. Watts, R. C. Purdy and co-workers, W. A. Hull, W. A. Lethbridge, L. Petrik, and T. Leykauf—*vide infra*, stannic chromate. C. W. Stillwell said that the red colour of rubies is not due to colloidal chromic oxide; that it is not due to higher or lower oxides of chromium; nor to variations in the proportion of chromic oxide present. He assumed that the red colour is due to a second modification of chromic oxide, of the same crystal structure as the green modification and alpha alumina, whose axial ratio is nearer to that of alpha alumina than is the axial ratio of the green modification. Therefore, the red modification tends to form when chromic oxide is added to alpha alumina and does form under ordinary conditions up to a certain point, beyond which the effect of the alumina is not strong enough to stabilize it. The occurrence of the red or green modification depends on the value of the axial ratio of the mixed crystal. There is a discontinuity in the change of the axial ratio with change in chromic oxide content when one modification changes to the other. There is also a marked difference in the axial ratio of a mixed crystal containing the red form of chromic oxide and a crystal containing the same amount of chromic oxide in the green form. This change in axial ratio may be affected in two different ways—*e.g.* by varying the proportion of chromic oxide, or by varying the nature of the atm. in which the mixture is fused.

L. Blanc showed that the blue, amorphous oxide, which he designates $\alpha$–$Cr_2O_3$, is rapidly transformed into the green, crystalline oxide—$\beta$–$Cr_2O_3$—at 700°. L. Blanc and G. Chaudron added that the exothermal passage of the blue, precipitated $\alpha$–$Cr_2O_3$ to olive-green $\beta$–$Cr_2O_3$, occurs at 500° in air and at 750° in vacuo. The blue

oxide absorbs oxygen rapidly at 200°, forming $CrO_2$ and $Cr_5O_9$. Both these form $\beta$–$Cr_2O_3$ and a black oxide at 440°, and if kept several hours at 350°, a larger proportion of the black oxide is formed. It is decomposed at 450°–500° yielding $\beta$–$Cr_2O_3$. Guignet's green, or finely divided $\beta$–$Cr_2O_3$, gives the black oxide on oxidation. Hence there are two oxides of the formula $Cr_5O_9$ with a transition temp. If the amorphous chromic oxide be heated in a gas-blowpipe, and cooled, E. Frémy, and M. Z. Jovitschitsch said that the product is crystalline ; and H. Moissan, also, by heating the oxide in the electric arc-furnace. T. Sidot crystallized the oxide by heating it in a current of oxygen ; J. J. Ebelmen, by strongly heating it with calcium carbonate and boric oxide ; and P. Ebell, by dissolving the oxide in molten glass at a high temp.—the oxide crystallizes out as the glass is slowly cooled.

Crystalline chromic oxide forms lustrous black **crystals,** or a green powder. According to G. Strüver, the trigonal crystals have the axial ratio $a : c = 1 : 1{\cdot}3770$, and $\alpha = 85° 22'$. The crystals were also examined by G. Rose, W. H. Miller, W. P. Blake, and J. J. Ebelmen. The **cleavage** on the (100)-face is well-defined. According to G. Rose, the crystals are isomorphous with the corresponding aluminium and ferric oxides. W. P. Davey found that the **X-radiograms** correspond with a diamond lattice except that the cube is stretched along its body-diagonal. The side of the unit triangle is 4·745 A. ; and the high axial ratio, 2·764, is explained by assuming a hexahedral molecule consisting of an equilateral triangle of oxygen with a metal atom immediately above and below the centre of the triangle ; there are three molecules per unit prism—**5**. 33, 10. W. H. Zachariasen made observations on this subject and obtained for the axial ratio $a : c = 1 : 1{\cdot}374$ : and for the parameter $r = 5{\cdot}35$ A. L. Passerini gave for the hexagonal cell $a = 4{\cdot}950$ A., $c = 6{\cdot}806$ A. ; with $a : c = 1 : 1{\cdot}374$, $v = 143{\cdot}4 \times 10^{-24}$ c.c., and density 5·283 ; and for the rhombohedral cell, $a = 5{\cdot}38$ A., and $\alpha = 54° 50'$ ; whilst P. E. Wretblad gave for the hexagonal cell, $a = 4{\cdot}949$ A., $c = 13{\cdot}57$ A., $a : c = 1 : 2{\cdot}7412$, and $\alpha = 55° 11'$. L. Passerini, and V. M. Goldschmidt and co-workers studied the solid soln. with alumina, and with ferric oxide (*q.v.*). W. Müller said that the oxide prepared by reducing potassium chromate with dry—not moist—hydrogen chloride is quite different from the ordinary oxide, being greyish-green, composed of tube-like plates of the hardness of graphite.

F. Wöhler found the **specific gravity** of the crystalline oxide to be 5·21 ; L. Playfair and J. P. Joule gave 4·909 ; H. Schröder, 5·010 ; H. Schiff, 6·2 ; W. A. Roth and G. Becker, 5·20 to 5·21 at 21° ; and E. Wedekind and C. Horst, 5·21 ; L. Blanc found that the oxide calcined from 500° to 800° has a sp. gr. 5·033 ; at 820°, 5·110 ; at 1080°, 5·130 ; and when fused, 6·145. H. P. Walmsley gave 5·238 for the sp. gr. of the dispersed oxide ; and W. H. Zachariasen, 5·25, calculated from the X-radiogram data. W. Biltz and co-workers found the mol. vol. of chromic oxide in the spinels to be 28·9. F. Wöhler found that crystalline chromic oxide has a **hardness** great enough for it to scratch quartz, topaz, and hyacinth ; and G. Rose, and W. P. Blake found that it is as hard as corundum. O. Ruff and A. Riebeth discussed the **plasticity** of mixtures of the oxide with water, etc.

H. V. Regnault gave 0·1796 for the **specific heat ;** F. E. Neumann, 0·196 ; and H. Kopp, 0·177 for the crystalline oxide. A. S. Russell found 0·0711 for the sp. ht. between —191° and —80·3° ; 0·1474, between —76·5° and 0° ; and 0·1805, between 2·6° and 49·3° and for the **molecular heat,** 10·81 at —136° ; 22·40 at —38° ; and 27·4 at 26°. J. Maydel discussed some relations of the sp. ht. J. J. Berzelius, H. Moissan, and J. Weise observed that the precipitated hydrated oxide exhibits **calorescence** when heated—*vide* alumina, **5**. 33, 10—and at the same time becomes denser, and less soluble in acids. W. G. Mixter said that the glowing occurs between 500° and 610°. J. J. Berzelius, L. Wöhler, and K. Endell and R. Rieke gave 500° ; H. le Chatelier, 900° ; L. Blanc, 550° to 600° ; G. Rothaug, 420° to 680°, according as the precipitate is pulverulent or granular—and he added that particles may be projected from the crucible at this temp. H. Moissan, H. le Chatelier, and W. G. Mixter regarded the change as evidence of the passage

from one allotropic form to another. L. Wöhler found that the calorescence is independent of the surrounding atm. and the humidity. The temp. of calorescence is lowered by increasing the quanity of material. With 8 grms. of chromic oxide, the temp. in dry hydrogen is 530°–550°, although in air or oxygen it begins at 425° on account of the exothermal decomposition of the chromium dioxide which is formed. The calorescence is hindered by precipitation with ammonia from soln. containing sulphate, and favoured by a low conc. of the chromic salt soln. L. Wöhler and M. Rabinowitsch found that the thermal value of the calorescence is 8 to 11 cals. per gram according as the oxide is precipitated from conc. or dil. soln. The change to the sintered oxide by calorescence is never complete. The oxide formed with the greatest heat development is the best absorbent for *m*-nitrobenzoic acid. M. Siewert showed that the glowing temp. depends on the rate of heating; and L. Wöhler, that the glowing is increased by conditions which favour hydrosol formation in the preparation of the hydrated oxide; and it is greater in proportion to the adsorption capacity of the precipitate. This agrees with the hypothesis that the phenomenon is connected with the surface area of the particles, and is due to a sudden decrease in the large surface of the oxide prepared by precipitation. J. Böhm found that the X-radiograms of chromic oxide before and after the calorescence showed that the glowing is attended by the passage of the oxide from the amorphous to the crystalline state. E. D. Clark found that chromic oxide melts in the oxy-hydrogen blowpipe flame giving off white fumes, but without reduction; E. Tiede and E. Birnbräuer studied the action of high temp. on the oxide. H. Moissan melted it in the electric furnace. C. W. Kanolt gave 1990° for the **melting point** of chromic oxide. L. Elsner observed that chromic oxide volatilizes in the porcelain ovens—presumably at 1500°–1600°. I have noticed evidence of its volatilization in pottery ovens at as low a temp. as 1050°; and C. Zengelis obtained evidence of its volatilization at ordinary temp. W. R. Mott gave 3000° as an approximation to the **boiling point.** F. Born calculated the **dissociation pressure** of chromic oxide at 2000° to be 3 mm., and at 3000°, over 760 mm. H. von Wartenberg and S. Aoyama gave for the partial press. of the oxygen at 600° and 1130° respectively $p_{O_2}=6{\cdot}73\times10^{-37}$ and $3{\cdot}07\times10^{-13}$. W. G. Mixter gave for the **heat of formation** of crystalline chromic oxide $(2Cr,1\frac{1}{2}O_2)$ =267·8 Cals.; for the stable amorphous oxide, 266 Cals.; and for the unstable oxide, 243 Cals. H. von Wartenberg gave 265·8 Cals.; and W. A. Roth and G. Becker, 288·0 Cals. H. von Wartenberg and S. Aoyama calculated 279 Cals. The subject was discussed by H. Collins.

E. L. Nichols and B. W. Snow measured the **reflecting power** of chromic oxide; and M. Luckiesh found that for light of wave-length $\lambda$ in $\mu$:

| $\lambda$ | 0·44 | 0·48 | 0·54 | 0·56 | 0·60 | 0·64 | 0·70 |
|---|---|---|---|---|---|---|---|
| Light green | 10 | 14 | 23 | 20 | 11 | 9 | 6 per cent. |
| Medium green | 7 | 10 | 17 | 13 | 7 | 6 | 5 per cent. |

W. W. Coblentz found for the ultra-red reflecting power:

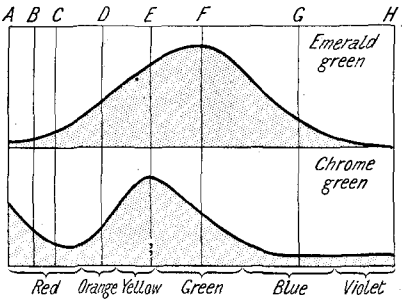
| $\lambda$ | 0·60 | 0·95 | 4·4 | 8·8 | 24·0$\mu$ |
|---|---|---|---|---|---|
| Reflecting power | 27 | 45 | 33 | 5 | 8 per cent. |

and for the **ultra-red emission spectrum,** he obtained for the diffuse reflecting power:

| $\lambda$ | 0·54$\mu$ | 0·60$\mu$ | 0·95$\mu$ | 4·4$\mu$ | 8·8$\mu$ | 24·0$\mu$ |
|---|---|---|---|---|---|---|
| Emission | 24·1 | 27·0 | 46·4 | 32·9 | 5·0 | 8·2 |

The results are illustrated by Fig. 15, where the green oxide furnishes a fairly smooth spectrum with a possible maximum at 5$\mu$, and a depression at 3·2$\mu$. H. Schmidt-Reps studied this subject. G. Liebmann found the emissive power for visible red-light between 1208° K. and 2000° K. decreases with decreasing grain-size; it is independent of temp.; and increases rapidly with decreasing wave-length—*e.g.* for green light.

A. Dufour examined the **flame spectrum**; K. Skaupy, the heat radiation from the incandescent oxide; and W. N. Hartley, the spectrum of the oxide in the oxy-hydrogen flame. G. H. Hurst showed that with emerald-green pigment nearly all the green rays are reflected and only a small proportion of other rays, Fig. 13, while with chrome-green pigment, the green rays are reflected nearly in their full intensity, Fig. 14, but there is also reflected a portion of the red, blue, and violet rays. Hence the deeper tone of chrome-green in comparison with emerald-green. T. Dreisch studied the ultra-red absorption spectrum of glass coloured with chrome oxide. R. Robl observed but a faint luminescence in ultra-violet light. H. S. Patterson and R. Whytlaw-Gray studied the photophoresis of chromic oxide aerosols; and R. Whytlaw-Gray and co-workers, and E. Thomson found that particles exhibiting the Brownian movement form chains in an electrostatic field. C. Doelter observed no coagulation in radium rays; W. P. Jorrissen and H. W. Woudstra also studied the phenomenon. J. Vrede found the oxide to be of no use as a **radio-detector**.




FIGS. 13 and 14.—Reflection Spectra of Emerald-green and Chrome-green.

E. Friederich calculated $2{\cdot}9\times10^{9}$ for the **electrical resistance** of a metre of wire 1 sq. mm. section. According to M. Faraday, and L. F. Nilson and O. Pettersson, chromic oxide is magnetic. S. Meyer found the **magnetic susceptibility** to be $X=24\times10^{-5}$ mass units at 17°; and E. Moles and F. Gonzalez, $26{\cdot}2\times10^{-6}$. Comparative measurements were made by P. Hausknecht. E. Wedekind and co-workers gave $25{\cdot}97\times10^{-1}$ mass units at 16°; L. Blanc and G. Chaudron found an abrupt increase at 880° followed by a fall at 900°. G. Chaudron and H. Forestier observed that the coeff. of susceptibility of calcined chromic oxide is greater than that of the uncalcined oxide. S. Veil studied this subject. K. Honda and T. Sone gave:

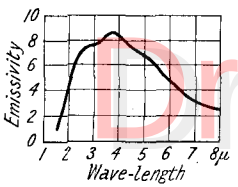



FIG. 15. — Ultra-red Emission Spectrum of Chromic Oxide.

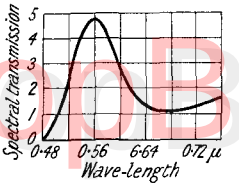



FIG. 16.—Spectral Transmission Factor of Chrome Green.

| | −186° | −64° | −3° | 17·6° | 64° | 117° | 644° | 1335° |
|---|---|---|---|---|---|---|---|---|
| $\chi\times10^{6}$ . . | 20·1 | 22·2 | 24·6 | 25·5 | 26·0 | 25·6 | 17·7 | 12·6 |

**The chemical properties of chromic oxide.**—E. D. Clarke said that chromic oxide is not decomposed by the oxyhydrogen blowpipe flame; and J. J. Berzelius found that it is not decomposed by **hydrogen** at a red-heat. For the electroxidation of chromic oxide, *vide* chromic acid, etc. According to R. Saxon traces of chromic acid are formed by the anodic oxidation of chromic oxide in pure water; the addition of manganese dioxide to the chromic oxide increases slightly the yield of chromic acid. Much more rapid oxidation ensues in the presence of calcium or potassium hydroxide or both. In soln. of alkali chlorides containing a little chrome-alum, chromic oxide is rapidly oxidized at the anode to chromic acid. K. Fischbeck and E. Einecke found that powdered chromic oxide is not perceptibly reduced when used as anode in the electrolysis of 2 per cent. sulphuric acid. The adsorption of hydrogen by the $ZnO$–$Cr_2O_3$ catalyst was studied by W. E. Garner and F. E. T. Kingman; whilst O. Schmidt, and A. F. Benton studied the adsorption of hydrogen by chromic oxide; and also the adsorption

of **oxygen**. H. N. Warren, and H. von Wartenberg found that chromic oxide is reduced to the metal by hydrogen at 5 atm. press., and at 2500° ; and E. Newbery and J. N. Pring, by hydrogen at 2000° and 150 atm. press. H. von Wartenberg and S. Aoyama found that whereas iron oxides are reduced at 1100° when $pH_2O/pH_2$ is about 1, this ratio must be about 0·001 for the reduction of chromic oxide. Hence, since water is produced in the reduction, an enormous excess of hydrogen would be needed to reduce any quantity of chromic oxide, and there is no possibility of such a process being used instead of the alumino-thermic process for preparing carbon-free chromium. The heat of reaction calculated from these results agrees with the value for the heat of formation of chromic oxide from chromium, and it is inferred that chromous oxide is not an intermediate stage at these temp. (600–1400°)—*vide supra*, chromium. H. Moissan found that when chromic oxide is heated in oxygen to about 440°, some chromium dioxide is formed which decomposes into ordinary chromic oxide at a higher temp. According to L. and P. Wöhler, no oxidation occurs when chromic oxide is heated to 1220°, and they suggest that the formation of higher oxides must be an endothermal process taking place at higher temp. If chromic oxide is heated along with potassium sulphate in an atm. of oxygen at about 1000°, an equilibrium press. is established, which increases when the temp. is lowered, and decreases when the temp. is raised. This is therefore a case of exothermic dissociation, and the equilibrium is probably : $2K_2SO_4+Cr_2O_3+3O \rightleftharpoons 2K_2SO_4+2CrO_3$. The value of the equilibrium press. at any temp. varies with the quantity of oxygen already absorbed, probably because at 1000° potassium sulphate is fused and keeps the complex compound in soln. G. Rothaug found that the formation of chromic chromate, $5Cr_2O_3+9O \rightleftharpoons 2Cr_2(CrO_4)_3$, is a maximum at 300° and can be observed at 100°. The rate of the oxidation falls rapidly to 400°, and after that proceeds slowly. R. Schwarz added that the ignition of chromic oxide is best carried out in a platinum crucible since the reducing gases passing through the platinum hinder the formation of the chromic chromate, $Cr_5O_{12}$. Chromic oxide is insoluble in **water**—for the hydrates, *vide infra*. The oxide which has not been heated above the temp. at which it caloresces is more chemically active than otherwise. Thus, M. Traube and others showed that the chromic oxide obtained at a low temp. dissolves slowly, if at all, in **acids**, but not so if the oxide has been heated to a high temp. H. le Chatelier gave 900° as the temp. at which chromic oxide becomes insoluble in acids. A. Mailfert observed that **ozone** oxidizes chromic oxide. H. Moissan found that at 400°, moist **chlorine** reacts with dry chromic oxide forming chromyl chloride ; and R. Weber found that if the oxide has been dehydrated below the temp. of calorescence, it is easily attacked by dry chlorine to form chromyl chloride ; the calcined oxide is attacked by chlorine at a red-heat. If the chromic oxide is mixed with carbon, and heated in a current of dry chlorine, chromic chloride is formed. H. Moissan observed that the calcined oxide is not attacked by chlorine or by **bromine ;** and J. Weise added that the calcined oxide can be dissolved by **hydrofluoric acid** if a trace of chromic anhydride is present. K. Fredenhagen and G. Cadenbach found chromic oxide to be indifferent towards hydrofluoric acid. The attack by chlorine was studied by R. Wasmuth. O. Ruff and H. Krug found that chromic oxide is attacked with incandescence by **chlorine trifluoride**. G. Gore observed that liquid **hydrogen chloride** does not dissolve any chromic acid during 6 days' digestion.

J. L. Lassaigne, and K. Brückner found that chromic oxide is not attacked by **sulphur** vapour at a white-heat. H. Moissan observed that the oxide which has not been heated to a high temp. forms chromic sulphide when heated to 440° in a current of **hydrogen sulphide ;** but the calcined oxide is not attacked by this gas. C. Matignon and F. Bourion observed that when the oxide is heated in a current of **sulphur monochloride** and chlorine, chromic chloride is formed ; and R. D. Hall obtained a similar product with sulphur monochloride alone. F. Bourion found that the reaction begins at about 400°. G. Darzens and F. Bourion found that **thionyl chloride** at 400° also converts the chromic oxide into the chloride. L. and

P. Wöhler observed that **sulphur dioxide** does not reduce the oxide at a red-heat; and L. and P. Wöhler and W. Plüddemann studied its catalytic action in the oxidation of sulphur dioxide. H. P. Cady and R. Taft found the oxide to be insoluble in liquid sulphur dioxide, while chromic oxide which has been calcined at a high temp. does not dissolve in **sulphuric acid.** J. Weise said that if a trace of chromic acid be present, chromic oxide passes into soln. T. Sabalitschka and F. Bull said that fusion with **sodium pyrosulphate** is the best way to bring ignited chromic oxide into soln.

H. C. Wolterick found that when a mixture of **nitrogen** and hydrogen is passed over chromic oxide at 550°, a little ammonia is formed, and, according to H. N. Warren, some nitride as well; O. Schmidt studied the adsorption of nitrogen by chromic oxide, and also of **ammonia**. J. E. Ashby found that heated chromic oxide favours the combustion of ammonia in air. D. Maneghini studied it as a catalyst in the oxidation of ammonia. F. Ephraim observed that chromic oxide is attacked by **sodium amide**. M. Z. Jovitschitsch found that chromic oxide dissolves when digested for 10 hrs. with fuming or conc. **nitric acid**; the calcined oxide does not dissolve in nitric acid. R. Weber found that if strongly heated with **phosphorus pentachloride** chromic oxide furnishes the chloride. C. Lefèvre studied the action of **alkali arsenates** on chromic oxide.

J. J. Berzelius found that chromic oxide at a white-heat is decomposed by **carbon**; and H. C. Greenwood added that the reaction begins at about 1180°—*vide supra*, chromium. R. E. Slade and G. I. Higson said that the equilibrium press. of the oxide in contact with carbon at 1292° is 6·2 mm., and at 1339°, 9·2 mm. O. Heusler found that the carbon monoxide press. between 1480° and 1801° increases from 18 to 760 mm. The energy consumption for the liberation of a mol of carbon-monoxide is 52·8 Cals. The equilibrium between 886° and 1096° is represented by $\log K=11{\cdot}375-11550p^{-1}$. J. F. Gmelin, F. Göbel, and I. L. Bell observed that chromic oxide is not reduced by **carbon monoxide,** and G. Charpy said that this gas does not act on chromic oxide at 1000°. K. Chakravarty and J. G. Ghosh studied its catalytic action on the reaction between carbon monoxide and hydrogen; and W. E. Garner and F. E. T. Kingman, the adsorption of the gas by the $ZnO$–$Cr_2O_3$ catalyst. O. Schmidt, and A. F. Benton studied the adsorption of carbon monoxide and of **carbon dioxide** by chromic oxide; and O. Schmidt of **ethane** and **ethylene.** E. Demarçay, and H. Quantin found that **carbon tetrachloride** reacts with chromic oxide at a red-heat forming chromic chloride, phosgene, and carbon dioxide. P. Camboulives said that the reaction occurs at 580°. H. Rose observed that **carbon disulphide** at a white-heat forms chromic sulphide (*q.v.*). A. Kutzelnigg observed no oxidizing action on a soln. of **potassium ferrocyanide**. J. Milbauer found that molten **potassium thiocyanate** forms the sulpho-salt $K_2Cr_2S_4$. J. E. Ashby, J. R. Huffmann and B. F. Dodge, W. E. Garner and F. E. T. Kingman, W. A. Lazier, and H. H. Storch observed the catalytic action of chromic oxide in the oxidation of **alcohol, ether,** and **volatile oils**. W. Eidmann found chromic oxide to be insoluble in **acetone**; and H. Bodenbender found it to be soluble in a soln. of **calcium sucrate**—a litre of a soln. containing 418·6 grms. of sugar and 34·3 grms. of calcium oxide dissolves 1·07 grms. $Cr_2O_3$; a litre of a soln. containing 296·5 grms. of sugar and 24·2 grms. of calcium oxide dissolves 0·56 grm. of $Cr_2O_3$; and a litre of a soln. with 174·4 grms. of sugar and 14·1 grms. of calcium oxide dissolves 0·20 grm. of $Cr_2O_3$. A. Löwenthal studied its catalytic action in the oxidation of hydrocarbons and alcohol; L. J. Simon, the oxidation of organic substances; M. R. Fenske and P. K. Frolich, the formation of alcohol from carbon monoxide and hydrogen; J. R. Hoffman and B. F. Dodge, the formation and decomposition of methanol; and A. E. Tschitschibabin, the reaction between ammonia and acetylene. The use of chromic oxide as a mordant in the dyeing of **wool, cotton,** and **silk** was discussed by L. Liechti and J. J. Hummel, and W. D. Bancroft. The last-named said that from dichromate soln. wool first adsorbs chromic acid and this is reduced to chromic oxide, which is the true mordant; within limits, increasing

the acid conc. increases the chromic acid taken up; chromic acid oxidizes organic compounds more readily in presence than in absence of wool; when wool is mordanted with chrome alum, a basic sulphate changing later to chromic oxide is first formed; silk adsorbs chromic oxide less strongly than wool does; cotton takes up scarcely any chromic oxide from chrome alum, but adsorbs it from an alkali soln.; there is no evidence of the formation of any definite compound when wool is mordanted with chromic oxide. A. W. Davison discussed the adsorption of chromic oxide by **leather**; H. Rheinboldt and E. Wedekind, the adsorption of organic dyes by chromic oxide.

A. Fodor and A. Reifenberg found that **silicic acid** peptizes ignited chromic oxide forming a colloidal soln. W. Guertler showed that the oxide is slightly soluble in molten **boric oxide** producing a green coloration. S. Kondo, and C. E. Ramsden examined the solubility of chromic oxide in pottery **glazes.** The reducing action of **boron** on heated chromic oxide was observed by A. Binet du Jassonneix; of **silicon,** by B. Neumann, and P. Askenasy and C. Ponnaz. L. Kahlenberg and W. J. Trautmann observed that when mixed with silicon, there is no reaction if heated by a bunsen burner, a slight reaction at a cherry-red heat, and a good reaction in the electric arc. E. N. Bunting studied the binary system of chromic oxide and **silica.** H. von Wartenberg and H. Werth found that when heated with **zirconia,** no compound is formed, but a eutectic appears at about 2200° with about 50 per cent. of chromic oxide.

The reducing action of **potassium** and **sodium** was observed by J. J. Berzelius; of **calcium,** by A. Burger; of **magnesium,** by J. Parkinson, and L. Gattermann—*vide supra,* chromium; of **aluminium**—*vide supra,* chromium; and the colouring effect on glass by K. Fuwa. For the action of **metal oxides,** *vide infra,* the chromites. H. D. Rankin got chromite into soln. by heating it to redness and afterwards treating it with alkali-lye under press. H. Schiff found that chromic oxide is attacked with difficulty by fused **potassium nitrate.** According to J. von Liebig and F. Wöhler, E. Bohlig, and F. H. Storer, chromic oxide is attacked and oxidized by fused **potassium chlorate, hydrosulphate,** and **permanganate;** by any suitable base in the presence of air or oxygen; and by **lead dioxide,** or **manganese dioxide** in the presence of sulphuric acid. For the action of permanganates, *vide* the permanganates. T. Sabalitschka and F. Bull said that chromic oxide is incompletely soluble in fused **potassium pyrosulphate;** to open the oxide up for analysis, it is preferable to fuse the substance with a mixture of 2 parts of sodium carbonate and 1 part of potassium nitrate for 10 min. The mass is dissolved in water and the insoluble residue fused with pyrosulphate. F. Hans found that chromic salts are oxidized by silver salts in accord with $Cr_2O_3+3Ag_2O=2CrO_3+6Ag$. J. Hargreaves and T. Robinson found that when mixed with **alkali chloride,** and heated in air or oxygen, chlorine is evolved, and in moist air, hydrogen chloride.

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## § 10. Hydrated Chromium Oxides. Chromium Hydroxide

Some of the *chrome ochres*—**6**. 40, 49—contain hydrated chromic oxide. According to W. Ipatieff and A. Kisseleff,[1] if $2N$-$H_2CrO_4$ at 240°–300° be exposed to hydrogen at 150° to 180° atm. press., a heavy, greyish-violet, slightly crystalline precipitate of **chromic oxyhydroxide,** $Cr_2O_3.H_2O$, or $CrO(OH)$, is formed; if in 25 c.c. of soln., 4 c.c. of $\frac{1}{10}N$-$H_2SO_4$ be present, in a gold tube, a similar violet-grey precipitate is formed at 300° to 325°; and in a quartz tube, the crystals are green, and cubic. If more sulphuric acid is present, at 300°, and 180 to 200 atm. press., two kinds of crystals are formed. According to W. Ipatieff and B. Mouromtseff, a nitric acid soln. of chromic nitrate when exposed to hydrogen at 320°–360°, under a press. of 200–370 atm., for 12–24 hrs., gives monohydrated chromium oxide closely resembling chrome ochre. If air is used in place of hydrogen, smaller crystals are obtained and the separation is not quantitative, a portion of the oxide being converted into chromic acid. Small amounts of dark red crystals are also occasionally obtained. According to J. B. Trommsdorff, if soln. of chromic salts are treated with alkali hydroxides, or aq. ammonia, it is best to work with boiling soln. It is difficult to wash the precipitated hydrated chromic oxide free from adsorbed salts. The product has been called **chromic hydroxide,** $Cr(OH)_3$, but it is generally supposed to be a colloidal hydrated oxide of less definite composition. O. Ruff and B. Hirsch studied the fractional precipitation of chromic

hydroxide in the presence of salts of other metals. S. Hakomori said that the reason ammonia does not precipitate hydrated chromic oxide in the presence of tartaric acid is because a complex salt is formed; and not in the presence of glycerol, because of colloidal phenomena induced by the high viscosity of the soln. The complex tartrate-ions were studied by K. Jellinek and H. Gordon.

J. J. Berzelius obtained a similar product by boiling a mixed soln. of potassium chromate and pentasulphide; G. F. C. Frick, by boiling a soln. of potassium chromate with sulphur; G. Lösekann, by the action of hydrogen sulphide on an alkaline soln. of a chromite oxide; H. Baubigny, by the action of hydrogen sulphide on a soln. of potassium dichromate; J. Casthelaz and M. Leune, by the action of zinc hydroxide, carbonate, or sulphide, or of aluminium hydroxide, or of zinc in a feebly acid soln. of green chromic chloride; and K. Seubert and A. Schmidt, by the slow action of magnesium on a warm soln. of a chromic salt. P. A. Thiessen and B. Kandelaky prepared the hydroxide free from adsorbed electrolytes by the hydrolysis of chromic ethylate: $2Cr(OC_2H_5)_3+6H_2O=Cr_2O_3.3H_2O+6C_2H_5OH$. A. Simon and co-workers used P. A. von Bonsdorff's process for hydrated alumina, and treated a soln. of the hydroxide in soda-lye with freshly precipitated, hydrated oxide, and after washing with water, and drying with acetone obtained a product with $Cr_2O_3.5{\cdot}68H_2O$. B. Schwarz obtained the hydroxide by the hydrolysis of chromites. V. Ipatéeff produced crystals of the hydrated oxide by heating soln. of the salts at high temp. and press. A. C. Becquerel obtained crystals of the hydroxide by suspending a parchment paper tube containing a conc. soln. of potassium aluminate in a soln. of chromic chloride. J. Férée obtained what he regarded as a monohydrate $Cr_2O_3.H_2O$, or $Cr(OH)O$, as a black, amorphous powder by the electrolysis of a neutral soln. of chromic chloride with a platinum cathode. This subject has been previously discussed in connection with R. Bunsen's, and J. Voisin's observations on the electro-deposition of chromium. G. B. Frankforter and co-workers heated a mixture of potassium dichromate and ammonium chloride to 260° and obtained a slate-coloured residue which, on lixiviation with water, left small, greenish-black, iridescent spangles of what has been thought to be a *dihydrate*, $Cr_2O_3.2H_2O$, or $Cr_2(HO)O$.

Analyses of the hydrates of chromic oxide vary very much. According to M. Siewert, the precipitate which has stood for some hrs. in air at 45° for 3 hrs. has $5{\cdot}9\ H_2O$; 3 hrs. at 100°, $5{\cdot}2H_2O$; 4 hrs. at 100°, $4{\cdot}8H_2O$; 2 hrs. at 105°, $4{\cdot}2H_2O$; 2 hrs. at 150°, $3{\cdot}2H_2O$; 5 hrs. at 200°, $2{\cdot}3H_2O$; and 6 days at 220°, $1{\cdot}1H_2O$. L. Schaffner obtained for the ammonia-precipitate dried over sulphuric acid, $6H_2O$; and dried at 100°, $5H_2O$; the alkali-precipitate dried at 100°, $4H_2O$. A. J. W. Forster gave for the air-dried, ammonia-precipitate $Cr_2O_3.8H_2O$. E. Frémy found for the potash-precipitate obtained in the cold, and dried in air, $9H_2O$, and that obtained from a boiling soln., and dried in air, $8H_2O$. J. Lefort, and A. Schrötter obtained similar data. C. F. Cross represented the composition of the precipitate dried at 100° by $Cr_2O_3.4H_2O$, and after standing in air sat. with moisture, $Cr_2O_3.7H_2O$, and after heating to dull redness, $Cr_2O_3.3H_2O$. M. Prud'homme gave $Cr_2O_3.5H_2O$ for the precipitate dried at 100°. G. Wyrouboff gave $Cr_2O_3.8H_2O$ for the precipitate dried over sulphuric acid, and $Cr_2O_3.6H_2O$ when dried at 110°. According to H. Löwel, the red-coloured ammonia-precipitate which dissolves in ammonia forming a red soln. is a different hydroxide from the bluish violet-coloured hydroxide, and this again is different from the green-coloured hydroxide. J. Lefort, E. Frémy, and J. M. Ordway also regarded the differently coloured hydroxides as isomers. According to A. Recoura, chromic hydroxide exists in three different molecular conditions. The first is obtained by precipitating a soln. of either variety of chromic chloride or of any violet chromium salt with an eq. quantity of sodium hydroxide. If treated with hydrochloric acid immediately after precipitation, it combines with 6 mols. of HCl with the development of 41·4 cals. The second variety is obtained by precipitating the oxychloride $Cr_2Cl_4O$

with 4 mols. of sodium hydroxide. Immediately after precipitation, it combines with 4 mols. of hydrochloric acid only, with development of 24·2 cals. The subsequent addition of a further quantity of 2 mols. of acid produces no thermal disturbance. The third form is obtained when either of the preceding varieties is dissolved in the necessary excess of soda-lye (18 mols. in the first case, 6 mols. in the second), and reprecipitated by neutralizing the excess of alkali. It combines with only 4 mols. of hydrochloric acid, with development of 20·0 cals. A. Colson assumed that there are hydroxides corresponding with the green and violet sulphates. He supposed that the green sulphate corresponded with

$$(OH)_2{=}Cr{-}O{-}Cr{=}(OH)_2$$
$$(OH)_2{=}Cr{-}O{-}Cr{=}(OH)_2$$

This formulation for hydrated chromic oxide—*i.e.* $Cr_4(OH)_8O_2.10H_2O$, or $Cr_4(OH)_{10}{\cdot}0{\cdot}9H_2O$—was favoured by M. Z. Jovitschitsch. G. Wyrouboff supposed the violet hydroxide is constituted $Cr_2(OH)_6$, and the other hydroxide $Cr_2(OH)_4(OH)_2$, or $Cr_2O(OH)_2$, where the two OH-groups can function as an acid. Although J. J. Berzelius assumed that the oxides precipitated from violet and green soln. of chromic chloride are isomers because they gave the soln. the original colour when dissolved in acids, yet the observations of A. Recoura indicate that the hydrated oxides from differently coloured soln. are the same in chemical structure. The individual variation depends on differences in the physical character of the particles. The rate of precipitation was shown by J. Casthélaz and M. Leune, and H. B. Weiser to have a marked effect on the colour. When slowly precipitated, the oxide is dark green and granular, and when rapidly precipitated greyish-blue and gelatinous. P. Bary and J. V. Rubio found that the dried hydroxide is heterogeneous, for it contains two products. R. Fricke and F. Wever could detect no evidence of crystal structure by X-radiograms.

N. Bjerrum measured the potential of the hydrogen electrode immersed in soln. of chromic chlorides, and inferred that the violet chromic chloride is progressively hydrolyzed, $CrCl_3 \rightarrow CrCl_2(OH) \rightarrow Cr(OH)_2Cl \rightarrow Cr(OH)_3$. He considered that freshly precipitated chromic hydroxide, $Cr(OH)_3$, is a well-defined chemical compound with a solubility product of $4{\cdot}2\times10^{-16}$ at 0° and $5{\cdot}4\times10^{-16}$ at 17°. On the other hand, J. M. van Bemmelen observed that the bluish colloid, prepared by treating a dil. soln. of a chromic salt with ammonia at the ordinary temp. or at 100°, contains originally 11 mols. $H_2O$; after exposure to the air at 15° it contains 7·8 to 8 mols.; but after keeping for 14 days in an atm. sat. with moisture the quantity of water rises to 13·2 mols., and after exposure to dry air it falls to 7·0 mols. When heated in the air at temp. increasing from 45° to 200°, the amount of water falls from 5·9 to 2·3 mols., and the colour changes to a dirty green. The results obtained on heating at temp. varying from 15° to 100° (i) in a sat. atm., (ii) in ordinary air, and (iii) in dry air, until the weight is constant, show that at every temp. equilibrium is established between the vap. press. of the colloid and that of water at the same temp. At 65° and at 100°, it retains more water in a sat. atm. than at 15° and 65° respectively in a dry atm. After having been heated at from 15° to 100° in dry air, its absorptive power is only slightly diminished, and at higher temp. it retains more water than colloidal silica, alumina, stannic acid or ferric oxide at the same temp., but the higher the temp. to which it has been exposed, the more insoluble it becomes in acids and especially in alkalies. He therefore inferred that colloidal chromic oxide has no definite composition at any temp. between 15° and 280°. This conclusion was confirmed by A. L. Baykoff, and H. B. Weiser. R. Fricke examined the X-radiogram of the hydroxide. S. Veil studied the effect of chromic hydroxide on the decomposition of hydrogen dioxide. H. J. S. King prepared **chromic pentamminohydroxide,** $Cr(OH)_3.5NH_3$, or **chromic hydroxypentamminohydroxide,** $[Cr(NH_3)_5(OH)](OH)_2$, by triturating chromic chromopentamminochloride with moist silver oxide, as indicated by O. T. Christenson. Similar results were obtained by using chromic aquopentamminochloride.

L. Havestadt and R. Fricke studied the dielectric constant. The electrical conductivity, $\mu$ mhos, for soln. with a mol of the salt in $v$ litres of water at 0°, and the calculated percentage degree of ionization, $\alpha$, are :

| | | | | | | |
|---|---|---|---|---|---|---|
| $v$ | 22·53 | 32·85 | 42·92 | 65·70 | 365·8 | $\infty$ |
| $\mu$ | 237·8 | 245·5 | 250·0 | 254·1 | 273·7 | 283·9 |
| $\alpha$ | 83·8 | 86·5 | 88·1 | 89·5 | 96·4 | |

Hydrated chromic oxide can be obtained in various shades of colour ranging from a clear greyish-blue to a dark green. Some of these are utilized as permanent pigments. The so-called *Guignet's green* has attracted some attention. This vivid, green pigment was prepared by E. Guignet by heating a mixture of potassium dichromate with three times its weight of boric acid, digesting the product with water, and washing it with water. Modifications of the process were described by A. Salvétat, M. Poussier, and A. Scheurer-Kestner ; L. Wöhler and W. Becker, in agreement with A. Scheurer-Kestner, said that boron is without influence on the colour, and that the trace of boron present is derived from the chromium borate first formed and subsequently hydrolyzed. If ammonium dichromate is employed in place of potassium dichromate, not a trace of boron remains after the washing, and when dried at 110°, the product has the composition $2Cr_2O_3.3H_2O$, or $Cr_4O_3(OH)_6$, ascribed to it by A. Scheurer-Kestner, and E. Guignet. A. Salvétat gave $Cr_3O_3.2H_2O$ ; A. Eibner and O. Hue, $2Cr_2O_3.5H_2O$ ; and M. Shipton considered it to be a borate, $3Cr_2O_3.B_2O_3.4H_2O$. According to L. Blanc, Guignet's green is not a hydrate, but very finely-divided chromic oxide, which, when heated in air, or treated with chromic acid, forms $\beta$-$Cr_5O_9$. L. Wöhler and J. Dierksen observed that when the green is produced by fusing potassium dichromate with boric acid, the failure to convert the dull olive-green to the brilliant green pigment by heating with water under press. supported the view that the complex $Cr_2O_3.3B_2O_3$ is responsible for the colour, but boric oxide is not a necessary constituent of the bright green. They suggest that the bright green has a gel-structure ; X-radiograms show that a lattice structure is absent. The reduction of the amount of water in chromium hydroxide gels with an increase in the size of particles progressively increases the brilliancy of the product. Boric acid and silicic acid are effective in producing the required flocculation. The vap. press. of brilliant flocculated hydroxides is greater than that of the dull non-flocculated hydroxides of the same water-content. L. Blanc and G. Chaudron found that Guignet's green yields a black oxide, $Cr_5O_9$, when heated. L. Wöhler and W. Becker said that a green pigment resembling Guignet's green can be obtained by heating the ordinary oxide with water under press. at 180° to 250°. The composition approximates $2Cr_2O_3.3H_2O$. Whilst Guignet's green has a vap. press. of 13 mm. at 75°, 16 mm. at 81°, and 26 mm. at 86°, the greyish-violet chromium hydroxide, which has the same composition, is found to have a vap. press. of only 2 mm., not increasing between 75° and 93·4°. This small vap. press. may result from the presence of moisture. These differences and the difference in colour of the two hydrates are ascribed to isomerism. The greyish-violet hydroxide is converted into its brilliant green isomeride on prolonged heating with water at 250°. H. B. Weiser added that the amorphous, hydrated oxide, obtained by precipitation, loses water continuously, and while it may be possible to dry the pigment under conditions such that the composition may be expressed by a single formula, yet this does not prove that a true hydroxide is formed. There is no evidence of an inversion temp. in the passage from one coloured variety to that of another colour ; and H. B. Weiser observed that when a soln. of chromic chloride is treated with just enough sodium hydroxide for complete precipitation the precipitate obtained at 0° is greyish-blue ; that at 50°, greenish-blue ; that at 100°, bluish-green ; that at 150°, green with a bluish tinge ; that at 200°, clear green ; and that at 200°–325°, bright green. The time of heating was 30 min. except in the last case when the heating occupied 15 hrs. Hence the colour varies continuously

from greyish-blue to clear green as the temp. of precipitation rises; this shows that the colours are not due to isomers, but rather to differences in the sizes of the particles, the structure of the mass, and to the amounts of water enclosed under different conditions of formation. As the temp. of precipitation rises, the oxide becomes less gelatinous, less soluble in acids, and less readily peptized by alkalies. For the solubility of chromic hydroxide in alkali-lye, *vide infra*, chromites.

Hydrated chromic oxide freshly precipitated from cold soln. of a chromic salt by an alkali hydroxide or ammonia, is readily soluble in acids, and readily peptized by alkali hydroxides. The hydrated oxide, however, gradually suffers a change in physical character on *ageing*, and it then becomes far less soluble and far less chemically active. The process of ageing is attended by the growth of aggregates of the primary colloidal particles. The velocity of change is accelerated by raising the temp., or by the use of a medium with a slight solvent action. A. Recoura measured the molar heat of soln. in hydrochloric acid with an oxide precipitated by adding an acid to a colloidal soln. in alkali-lye, and kept for definite intervals of time. Thus, the mol. ht. of soln. in cals. of the freshly precipitated oxide is 20·70; when kept 10 min., 19·0 cals.; 1 hr., 5·80 cals.; 2 hrs., 3·90 cals.; 4 hrs., 2·85 cals.; 7 hrs., 2·40 cals.; 1 day, 1·75 cals.; 7 days, 1·20 cals.; 30 days, 0·75 cal.; and 60 days, 0·50 cal. F. Bourion and A. Sénéchal observed that the rate at which hydrated chromic oxide reduces hydrogen dioxide becomes less on standing. The reaction appeared to be quadrimolecular for the first 8 hrs., due, it was supposed, to the transformation of the original oxide into complexes, so that the soluble and insoluble varieties represent definite allotropic forms. R. Fricke and O. Windhausen attributed the ageing to an increase in the size of the particles, and showed that it is not due to dehydration, or to the development of a microcrystalline structure. R. Fricke and co-workers observed no evidence of a crystalline structure in the ageing of hydrated chromic oxide. A. Simon and co-workers studied the vap. press. of the hydrated oxide. The continuous curve, Fig. 17, was obtained with a preparation precipitated by ammonia, washed with water at 60°, then with acetone, and dried in air. Its composition approximated $Cr_2O_3.6{\cdot}68H_2O$. This curve shows a slight flattening with the tri- and mono-hydrate. The other curve is obtained with a specimen precipitated by hydrazine, washed, and dried over sulphuric acid in vacuo for 8 weeks when its ocmposition was $Cr_2O_3.4{\cdot}87H_2O$. The formation of the tri- and mono-hydrates is clearly shown.

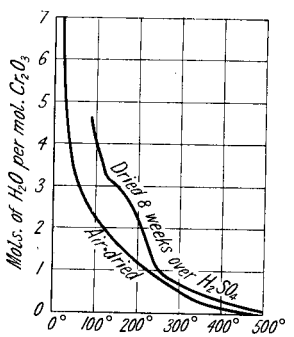


FIG. 17.—The Vapour Pressure of Hydrated Chromic Oxides.

M. Siewert showed that when the hydrated oxide is heated to 200°, in air, it takes up oxygen forming a black powder of variable composition, and it is regarded as a mixture of chromic oxide, chromic anhydride, and water. M. Krüger first observed the tendency of the hydrated oxide to take up oxygen when heated. A. Geuther showed that when the hydrated oxide is deposited on the negative pole, it is liable to form chromic anhydride by taking up oxygen. M. Z. Jovitschitsch found that hydrated chromic oxide readily absorbs carbon dioxide from the atm. forming $[Cr_2(OH)_5]_2CO_3.8H_2O$. The light grey hydrated chromic oxide which is precipitated with small quantities of ammonium hydroxide dissolves in an excess of ammonia to form a ruby-red soln. whose solubility is affected by the presence of ammonium salts. If the red soln. is kept for some time, M. Z. Jovitschitsch observed that violet-blue **chromium diamminohydroxide,** $Cr_2(OH)_6.(NH_3)_2.10H_2O$, is precipitated; it readily absorbs carbon dioxide.

A. Recoura gave for the heat of neutralization of hydrated chromic oxide with hydrochloric acid $\frac{1}{3}Cr(OH)_3$=6·865 Cals.; E. Petersen, with hydrofluoric acid,

8·39 Cals.; and M. Berthelot, with sulphuric acid, $\frac{1}{2}H_2SO_4$, 8·22 Cals. W. Pauli and E. Valko studied the conductivity and activity coeff. H. R. Robinson and C. L. Young studied the absorption frequency of the K-series of X-ray spectrum. L. Havestadt and R. Fricke studied the dielectric behaviour of the hydroxide; and H. R. Robinson and C. L. Young, the X-ray absorption frequencies. F. Bourion and A. Sénéchal found that the paramagnetism of an alkaline soln. of chromic oxide diminishes slowly with time, but the diminution is small, and never exceeds 20 per cent. S. Veil found that the magnetic properties of chromic hydroxide are decreased by heating it with water in a sealed tube between 120° and 210°; and another 12 hrs.' treatment has little effect, but when the hydroxide is dissolved in hydrochloric acid, and reprecipitated, the modified magnetism persists and a further change occurs by a similar treatment with hot water. T. Ishiwara found the magnetic susceptibility at 15·7° to be $66·2\times10^{-6}$ mass units, and at −68·3°, $110·5\times10^{-6}$ mass units. P. Hausknecht, and E. Wedekind and W. Albrecht observed that the magnetic susceptibility of $Cr(OH)_3$ is greater than that of the corresponding oxide, in agreement with the assumption that the hydroxide is a chemical individual. S. Veil found that the magnetic properties of chromic hydroxide fall to a lower limiting value on repeated precipitation from hot soln.

T. Graham prepared a positive **colloidal solution** of hydrated chromic oxide by peptizing the freshly precipitated oxide with chromic chloride, and dialyzing the liquid to remove the excess of electrolyte. The dark green soln. can be diluted with water or heated, but it is readily flocculated by electrolytes. In continuous dialysis, the diffused liquid was kept at a constant level and not changed during the process, whereas in intermittent dialysis, the diffusate was continuously changed at the rate of 800 c.c. per hour. M. Neidle and J. Barab found that some colloidal particles do diffuse through the parchment membrane; although W. Biltz, and H. W. Fischer and W. Herz observed no such diffusion. In the dialysis of hydrated chromic oxide in a soln. of chromic chloride, the ratio $\frac{1}{3}Cr:Cl$ in the diffusate, with intermittent dialysis, is always greater than unity, and this the more the longer the period of dialysis for the same diffusate. In continuous dialysis, the ratio $\frac{1}{3}Cr:Cl$ in the diffusate increases from unity to a maximum of 1·57, and then gradually diminishes towards zero. In intermittent dialysis, about 6 per cent. of the original colloid is still associated with considerable electrolyte, and it remains in the membrane at the end of 56 days; but the colloid still diffuses so that by continuing the process, the whole of the colloid would be removed from the membrane. In the continuous dialysis, 75 per cent. of the original colloid remains in the membrane. Continuing the process for 35 days increases the purity of the colloid without loss of chromium. If the intervals in intermittent dialysis are made smaller, more satisfactory results are to be expected. In fact, by conducting the entire process in very short intervals, the efficiency may even exceed that of continuous dialysis. The latter procedure is, however, impractical. The variations in the ratio of $\frac{1}{3}Cr:Cl$ in the diffusates are accounted for by the assumption of a gradual growth of the particles. In the intermittent process, the particles do not grow sufficiently to be retained by the membrane, whereas in the continuous process they do. A. Simon and co-workers used the dialyzer recommended by A. Gutbier and co-workers. The process of dialysis was studied by N. Bjerrum by measuring the osmotic press. of the colloidal soln. It is hence calculated that the colloidal chromium particle consists of 1000 chromium atoms and carries 30 free charges. The number of chromic oxide molecules in a colloidal particle is about 240. For complete coagulation the necessary amount of ferrocyanide corresponds exactly with the total charge on the colloid, whilst about 15 per cent. excess of ammonium or potassium sulphate is required. The commencement of coagulation is marked by a sudden break in the curve obtained by plotting conductivity against c.c. of ammonium sulphate. The subject was discussed by A. Lottermoser and W. Riedel, and H. Rinde. R. Wintgen and W. Biltz gave 580 for the number of chromic oxide molecules in a colloidal particle

aged by boiling, and 750,000 for the case of an aged ferric oxide colloidal particle. These numbers are of doubtful accuracy. J. R. I. Hepburn found that the product obtained after a prolonged freezing is colloidal in nature, but has some properties usually regarded as characteristic of the crystalline state. J. H. Yoe and E. B. Freyer measured the $H^{\cdot}$-ion conc. and viscosity of hydrosols of chromic oxide; D. N. Chakravarti and N. R. Dhar, the viscosity of the sol in the presence of electrolytes; E. Manegold and R. Hofmann, the permeability of membranes for the hydrosol; and S. Horiba and H. Baba, the effect of light on the osmotic pressure of the hydrosol.

C. Paal prepared a colloidal soln. of hydrated chromic oxide by reducing a soln. of ammonium chromate with colloidal platinum in the presence of sodium protalbinate which acts as a protective colloid. The colloid may be partially purified by dialysis. Soln. of aluminium or ferric salts give a precipitate of hydrated oxide when boiled with sodium acetate; but with chromic acetate soln., H. Schiff, and B. Reinitzer obtained no precipitate when the soln. was boiled; nor was a precipitate obtained in the cold with alkali hydroxide, ammonia, ammonium hydroxide or carbonate, sodium phosphate, or with barium hydroxide or carbonate. Except in the case of sodium phosphate, these reagents give precipitates with boiling soln. There is a slow action between chromic salt and sodium acetate in the cold, for, on standing some time, in the presence of alkali, the colour of the liquid changes and a jelly is formed. In the case of a boiling soln. of hydrated chromic oxide and sodium acetate, the precipitate formed is probably a complex acetate. Iron and aluminium acetates associated with violet chromic acetate do not give a precipitate when boiled or when treated with alkali-lye or aq. ammonia. This, said H. B. Weiser, is not due to peptizing action of the adsorbed hydrated chromic oxide because hydrated chromic oxide is not the primary product of the hydrolysis of chromic acetate, and, as B. Reinitzer has shown, green chromic acetate does not prevent the precipitation of hydrated ferric oxide. The phenomenon as probably the result of the formation of the iron-chromic acetates was studied by R. F. Weinland and E. Guzzmann. The alleged formation of colloidal hydrated chromic oxide, by B. Reinitzer and H. W. Woudstra, by dialyzing soln. of chromic acetate, does not seem right since basic chromic acetates are probably produced. M. Neidle and J. Barab obtained no colloid by dialyzing chromic acetate soln. into which superheated steam was passed; nor was any obtained by the dialysis of a cold soln. of purified chromic chloride, although H. M. Goodwin and F. W. Grover obtained a little by the dialysis of the commercial ferric chlorides. W. Biltz obtained no colloid by the hydrolysis of soln. of chromic nitrate, owing to the small hydrolysis of the salt as observed by H. W. Woudstra. S. Takegami obtained the colloid at the cathode during the electrolytic reduction of chromic acid; and B. Kandelaky, by the hydrolysis of chromic ethylate.

H. W. Fischer studied the solubility of hydrated chromic oxide in a soln. of chromic chloride; R. Wintgen and H. Weisbecker, the amphoteric properties of the colloid; and P. Bary and J. V. Rubio, E. Manegold and R. Hofmann, and R. Wintgen and O. Kühn, the structure of the colloid. F. Haber showed that if the rate of aggregation of a colloidal sol is high, amorphous precipitates are to be expected which gradually, and particularly on warming, pass into the crystalline condition. If, however, the rate of aggregation is depressed by only slightly exceeding the solubility limit, the rate of arrangement may be sufficient to cause the orderly formation of crystals before the formation of visible particles has occurred. This, however, involves an alteration in the rate of aggregation due to electrical phenomena at the boundary of the molecules and liquid, the net result of which is that the growth of the aggregates is greatly impeded and sols are produced.

The colloidal soln. of hydrated chromic oxide prepared as just indicated was shown by W. Biltz, and W. Herz to be a **positive hydrosol** because it migrates to the cathode under the influence of an electrical stress. On the other hand, the

green colloidal soln. obtained by adding an excess of alkali hydroxide to a soln. of a chromic salt was found by R. Kremann to be a **negative hydrosol** because, under the influence of an electrical stress, it migrates to the anode. W. Reinders studied the electrophoresis of the colloid. The clear, negative colloidal soln. was found by H. W. Fischer and W. Herz to precipitate spontaneously on standing, particularly if the ratio of chromic oxide to hydroxide is large. This is due to the ageing of the hydrated oxide. A. Hantzsch also observed that owing to ageing, the precipitated and washed chromic oxide is not peptized by alkalies. The colloid is precipitated by adding electrolytes owing to the adsorption of the cations as observed by H. W. Fischer. A. Lottermoser found that the ultra-filtration of the chromic oxide sol peptized with the corresponding chloride gives a filtrate which contains hydrochloric acid of the same $H^{\cdot}$-ion conc. as that of the sol. The mycellia therefore retains the chloride ion whose negative charge compensates the positive charge of the colloidal particles. The conductivity of the sol is greater than that of the ultra-filtrate, and the difference is taken to represent the true conductivity of the mycelles which are regarded as complex electrolytes. A. B. Dumansky and co-workers studied this subject. R. Fricke and co-workers found tetramethylammonium hydroxide to be a strong peptizing agent.

C. F. Nagel, W. D. Bancroft, and N. G. Chatterji and N. R. Dhar showed that the colloidal oxide can be removed by the ultra-filter. W. Biltz and W. Giebel added that the colloidal soln. consists mainly of amicrons, only a small proportion of sub-microns are present. There has been some discussion as to whether the colloidal soln. contains alkali chromite. H. W. Fischer and W. Herz said that peptization, not dissolution, occurs. This is in agreement with hypothesis that the soln. is really the colloidal oxide and the observation of A. B. Northcote and A. H. Church that complete soln. occurs in the presence of 40 per cent. of ferric oxide; 12·5, manganous oxide; or 20 per cent. of either cobalt or nickel oxide, whereas complete precipitation occurs with 80 per cent. of ferric oxide; 60, of manganous oxide; or 50, of either cobalt or nickel oxide. Analogous observations were made by M. Prud'homme, and M. Kreps. H. B. Weiser and G. L. Mack obtained an **organosol** in propyl alcohol.

According to C. F. Nagel, when an excess of potassium hydroxide is added to a soln. containing varied proportions of ferric chloride and chromic sulphate, the iron is not precipitated in presence of excess of the chromic salt, and the chromium is completely precipitated with the iron when the ferric salt is present in considerable excess. It is supposed that these effects are due to mutual adsorption. In a similar way, the hydroxides of manganese, cobalt, nickel, copper, and magnesium are absorbed by colloidal chromic hydroxide, whilst this is also adsorbed and removed from soln. by the above hydroxides when these are present in relatively large quantities. In presence of copper, chromium is not precipitated by ammonia, and it is suggested that this may be due to the presence of colloidal cupric hydroxide, which adsorbs the chromic hydroxide. The peptized soln. gradually settles leaving only a faintly coloured liquid; a collodion filter removes all the hydrated oxide leaving in soln. a little chromic chloride; and peptized hydrated chromic oxide cannot be extracted from soln. with benzene or light petroleum, but it goes into the dimeric interface. J. K. Wood and V. K. Black treated precipitated chromic oxide with varying proportions of a soln. of alkali hydroxide of varying concentration. The presence of chromate in the soln., after two months, indicated that some chromite had been formed; whilst a soln. of chromic chloride treated with a large excess of alkali-lye, after standing two months, gave a colloidal precipitate, and a yellow soln. of chromate formed by oxidation. They concluded that chromites do exist in an alkaline soln. of chromic hydroxide; when the soln. is freshly prepared and is kept a little time, part of the dissolved hydroxide separates out in a less soluble form, and probably does, during this period of transition, exist for a time in the colloidal condition, but when all such precipitation has taken place, a small amount of chromite will still be present in the soln.

According to E. Müller, when an excess of chromic oxide or hydroxide is shaken with aq. soln. of sodium hydroxide for several days, the solubility is dependent on the time of agitation, rising to a maximum and then falling to a constant value. Both the maximum and final solubilities attain their highest values at 14*N*-NaOH. It is assumed that chromium hydroxide is a " solid-liquid " in which simple and polymerized molecules are present in homogeneous soln. On account of the magnitude of the internal friction, equilibrium is only slowly attained. The ageing process does not so much consist in the enlarging of single particles as in a progressive change during polymerization and is thus essentially chemical in character. H. B. Weiser added that even if chromic oxide does possess slightly acidic properties, not all the oxide is present as chromite ; and it is doubtful if any chromite is present when slightly more alkali-lye is present than is needed to precipitate the chromic oxide completely. H. N. Holmes and M. A. Dietrich observed that mercuric sulphide is not precipitated by hydrogen sulphide from a 0·5*N*-hydrochloric acid soln. containing green chromic chloride and mercuric chloride in excess of the ratio 2 : 1, but is adsorbed by the colloidal chromic hydroxide produced by the hydrolysis of the chloride. The hydrolysis increases on keeping, and after 48 hrs. precipitation does not occur when the above ratio is 1 : 3·5, but this ratio may be depressed by a sufficient concentration of hydrogen or sulphate ions. Thus, chromic sulphate has no influence on the precipitation. The formation of colloidal chromic hydroxide is probably preceded by the conversion of the green chromic chloride into the violet form. The order of the adsorption is reversed by using a large excess of mercuric chloride and precipitating from a hot 0·5*N*-acid soln. K. C. Sen found that the absorption of acids by chromic oxide can be summarized in Fig. 18.

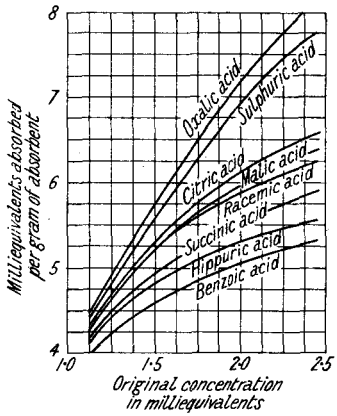


FIG. 18.—The Absorption of Organic Acids by Hydrated Chromic Oxide.

H. B. Weiser reported that the precipitation values for potassium salts for a negative colloidal soln. containing 365 grms. of chromic oxide per litre were for ferricyanide, 0·485 millieq. per litre ; chromate, 0·525 ; dichromate, 0·535 ; sulphate, 0·550 ; oxalate, 0·570 ; iodate, 0·635 ; bromate, 19·0 ; chloride, 30·0 ; bromide, 33·0 ; chlorate, 33·8 ; and iodide, 37·5. M. Bjerrum observed that by adding a soln. of 0·1*N*-ammonium sulphate to a soln. containing 0·112 mols of Cr, and 0·01 mol of nitric acid, the electrical conductivity of the soln. altered as indicated in Fig. 19. E. E. Porter measured the H·-ion conc. of a negative colloidal soln. of hydrated chromic oxide containing 2·5 grms. $Cr_2O_3$ per litre, when 5 c.c. were treated with 15 c.c. of a soln. containing salt and acid. A rapid precipitation of the colloid occurred when the $p_H$ was between 3·5 and 6·0. The flocculation of the colloidal soln. was also studied by A. Miolati and E. Mascetti, and N. Bjerrum, A. Ivanitzkaja and L. Orlova, S. L. Jindal and N. R. Dhar, K. Mohanlal and N. R. Dhar, W. V. Bhagwat and N. R. Dhar, S. Ghosh and N. R. Dhar, K. C. Sen and M. R. Mehrotra, K. C. Sen and N. R. Dhar, and R. Wintgen and H. Löwenthal. H. B. Weiser also studied the flocculation of a colloidal soln. of chromic oxide by mixed electrolytes ; and for the precipitation value of a negative colloidal soln.

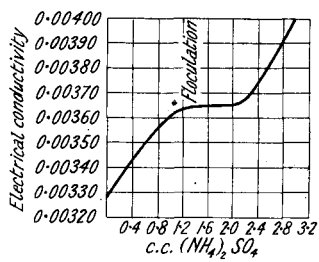


FIG. 19.—The Effect of Ammonium Sulphate on the Flocculation of a Colloidal Solution of Chromic Oxide.

obtained by adding 45 c.c. of 2*N*-KOH to 5 c.c. of a soln. of chromic chloride containing 40 grms. of chromic oxide per litre, the result with barium chloride was 5·15 millieq. per litre; potassium chloride, 500·0; sodium chloride, 210·0; lithium chloride, 51·0; sodium sulphate, 315·0; and sodium acetate, 220·0. S. Roy and N. R. Dhar studied the coagulation of the colloid in light. T. Katsurai observed that the hydrosol of chromic oxide does not coagulate like that of ferric oxide when heated under press.

B. Reinitzer prepared a **hydrogel** by boiling a soln. of a chromic salt and sodium acetate, rendered alkaline by alkali-lye or ammonia, and allowing it to set to a jelly. E. H. Bunce and L. S. Finch obtained a jelly by allowing a mixed soln. of alkali-lye and chrome alum to stand. They did not get the jelly by using soln. of chromic sulphate, nitrate, or chloride; but C. F. Nagel obtained the jelly with sulphate by keeping down the conc. of the alkali. H. B. Weiser observed that the rapid addition of a slight excess of alkali-lye to a soln. of chromic chloride produces a negative colloidal soln. which precipitates slowly forming a jelly; if the precipitation is hastened by heating the soln., or by adding a suitable amount of electrolyte, the precipitation is rapid and it is gelatinous but not a jelly; and finally, if the hydrated oxide has been peptized by a large excess of alkali, the precipitate forms slowly and is granular. R. Griessbach and J. Eisele obtained the gel by peptizing the hydrosol. J. Häusler and B. Kohnstein obtained the gel by separately atomizing an acid soln. of chromic acid and an alkaline soln. of sucrose in a mixing chamber, and recovering the colloidal hydroxide. D. N. Chakravarti and N. R. Dhar found that during dialysis of a hydrosol of hydrated chromic oxide, the liquid becomes more viscid and finally gelatinizes. S. Prakash and N. R. Dhar found that the soln. of 4 c.c. 0·5*M*-$CrCl_3$, and 8 c.c. of 3·57*N*-$CH_3.COONa$, mixed in half an hour with 2 c.c. of 2*N*-$(NH_4)_2SO_4$ and 5 c.c. of 2·34*N*-$NH_4OH$ added drop by drop, and the soln. made up to 20 c.c., sets to a jelly in 6½ hrs. at 30°. The viscosities of the soln. were:

| Age | 0 | 30 | 60 | 90 | 120 | 150 min. |
|---|---|---|---|---|---|---|
| Viscosity | 0·01465 | 0·01469 | 0·01527 | 0·01646 | 0·01873 | 0·02208 |

DropBooks

K. C. Sen and M. R. Mehrotra studied the peptization of chromic hydroxide by arsenious acid; and K. C. Sen, by sugar. S. G. Mokruskin and O. A. Esin examined the adsorption of aniline dyes by chromic oxide; N. Nikitin, the adsorption of ammonia; C. E. White and N. E. Gordon, and E. E. Porter, organic dyes; H. B. Weiser, oxalates; K. C. Sen, benzoic and acetic acids. They found that hydrated chromic oxide adsorbs acids and arsenious acid more than hydrated chromic or ferric oxides adsorbs arsenic trioxide; and N. R. Dhar and co-workers found that various metal salts—Zn, Cd, Co, and Ni—but not Ag salts, are adsorbed. According to E. Toporescu, when chromium is precipitated by ammonia from soln. of its salts containing calcium or magnesium, the amounts of these salts carried down increase with their concentration, and tend towards limits corresponding with the chromites, $Cr_2O_3.3CaO$ and $Cr_2O_3.3MgO$, respectively. The calcium or magnesium may be removed from such precipitates by washing them on the filter or by decantation with a boiling 5 per cent. soln. of ammonium nitrate. H. B. Weiser and E. E. Porter studied the effect of the $H^{\cdot}$-ion conc. of soln. on the adsorptivity of hydrated chromic oxide.

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## § 11. Chromites

Hydrated chromic oxide shows pronounced basic properties uniting with acids to form tervalent chromium salts. It is, however, an amphoteric oxide and it acts as a weak base forming salts—**chromites**—which have the spinel formula $RO.Cr_2O_3$, or $R(CrO_2)_2$. These salts can be regarded as **metachromites** derived from **metachromous acid,** $HCrO_2$, or HO.CrO; there are also indications of the formation of **orthochromites,** derived from **orthochromous acid,** $H_3CrO_3$, or $Cr(OH)_3$. According to F. Hein and H. Meininger,[1] chromium triphenylhydroxide $Cr(C_6H_5)_3OH$ is nearly as strong a base as sodium hydroxide. R. Wintgen and H. Weisbecker studied the amphoteric properties of chromic oxide hydrosol.

Z. Weyberg reported crystals of **lithium chromite,** $LiCrO_2$, to be formed along with lithium aluminate when mixtures of an excess of lithium chromate with china clay are calcined. The brown powder consists of microscopic, isotropic, octahedral crystals. As previously indicated, there are differences of opinion as to the nature of the green liquid obtained when freshly precipitated hydrated chromic oxide is treated with alkali-lye. The process is one of either peptization or dissolution; or else it includes both. R. Kremann, M. Kreps, and J. K. Wood and V. K. Black consider that the soln. of hydrated chromic oxide in alkali is chromite; while W. Herz and H. W. Fischer, A. Hantzsch, C. F. Nagel, W. V. Bhagwat and N. R. Dhar, and H. B. Weiser consider it to be peptized, hydrated chromic oxide. C. Fricke and O. Windhausen determined the solubility of hydrated chromic oxide approximating $Cr_2O_3.9H_2O$, expressed in grms. $Cr_2O_3$ per 100 c.c. of soln., after three days' digestion in a soln. of sodium hydroxide at ordinary temp. and obtained the following results:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *N*-NaOH . | 0·5 | 0·71 | 5·10 | 9·89 | 10·00 | 11·06 | 14·15 | 15·63 |
| $Cr_2O_3$ . | 0·25 | 0·5 | 1·58 | 2·89 | 2·68 | 1·90 | 0·80 | 0·40 |
| *K* or *K'* . | 3·6 | 3·4 | 3·2 | 3·4 | 2·7 | 2·6 | 2·3 | 1·5 |
| | $NaCrO_2$ | | | | $Na_3CrO_3$ | | | |

With 17·42*N*-NaOH, the soln. was almost colourless, $K=[NaOH]/[Cr]$, and $K'=[NaOH]^3/[Cr]$. The results are plotted in Fig. 20.

According to E. Müller, the equilibrium condition between a soln. of sodium hydroxide and chromic hydroxide is very slowly attained. The curves, Fig. 21, rise to a maximum and then fall to a minimum value, due, it is supposed, to the chromic hydroxide dissolving unchanged in the lye; it then changes by the loss of water into

a less soluble oxide, a change which is accelerated by heat. It is assumed that the equilibrium conditions are: $Cr(OH)_3 + 3NaOH \rightleftharpoons Na_3CrO_3 + 3H_2O$; $Cr(OH)_3 + 2NaOH \rightleftharpoons Na_2HCrO_3 + 2H_2O$; and $Cr(OH)_3 + NaOH \rightleftharpoons NaH_2CrO_3 + H_2O$; followed by $NaH_2CrO_3 + H_2O \rightleftharpoons NaCrO_2 + 2H_2O$. R. Fricke and O. Windhausen studied this subject and found that when hydrated chromic oxide is treated with sodium hydroxide, the formation of chromite precedes the formation of the hydroxide. With sodium hydroxide below 10*N*, primary sodium chromite is formed, whilst above 10*N* the soln. contains also tertiary sodium chromite. Potassium chromite is similarly produced; below 8*N*-alkali only the primary chromite is formed, whilst above 8*N* the soln. contains also secondary chromite. From soln. of potassium chromite which have stood for a long time, needle-shaped crystals of the formula $Cr_2O_3.3K_2O.8H_2O$ have been obtained. R. B. Corey found that the clear supernatant liquor left by chromic hydroxide settling from soda-lye contains no chromium, showing that chromic hydroxide is insoluble in that menstruum, and the apparent solubility is really peptization and not a case of soln. N. Demassieux and J. Heyrovsky inferred that soln. of alkali chromite are not true soln. but contain colloidal chromic hydroxide. The primary **sodium metachromite,** $NaCrO_2$, is formed with alkali-lye below 10*N*-NaOH; and **sodium orthochromite,** $Na_3CrO_3$, above that conc. J. d'Ans and J. Löffler obtained $NaCrO_2$ by the action of chromic oxide on sodium hydroxide. J. Heyrovsky obtained similar results

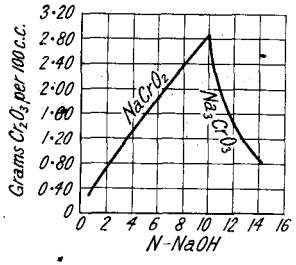


FIG. 20.—The Solubility of Hydrated Chromic Oxide in Solutions of Sodium Hydroxide.

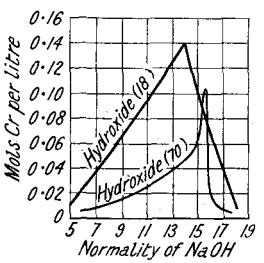


FIG. 21.—The Solubility of Chromic Hydroxide in Solutions of Sodium Hydroxide.

with potassium hydroxide as those obtained with soln. of sodium hydroxide; below 8*N*-KOH, only **potassium metachromite,** $KCrO_2$, is formed, and above that concentration, **potassium orthochromite,** $K_3CrO_3$. Z. Weyberg found that by melting mixtures of china clay and alkali chromate, chromic oxide first separates out, and afterwards the chromite. If the soln. of potassium chromite be allowed to stand for a long time, needle-shaped crystals of the tetrahydrate, $K_3CrO_3.4H_2O$, are deposited. These conclusions were confirmed by observations on the f.p., and potential of the soln. M. Kreps could not prepare potassium and sodium chromites in the dry way, because in subsequently washing out the excess of alkali with water, the chromite is decomposed. R. Kremann found that the movements towards the anode of the green soln. of hydrated chromic oxide in conc. alkali-lye demonstrates the existence of chromites; the hydrated chromic hydroxide is not present merely as a colloid because it can diffuse through parchment into the alkaline soln. H. P. Cady and R. Taft found potassium chromite to be insoluble in liquid sulphur dioxide. P. C. Boudault said that potassium ferricyanide oxidizes a soln. of potassium chromite to chromate. The salt is sparingly soluble in acids.

J. F. Persoz obtained **cuprous chromite,** $CuCrO_2$, by calcining cupric chromate in a crucible exposed to the reducing action of the furnace gases, and extracting the product with hydrochloric acid; and L. and P. Wöhler obtained it by heating one of the basic cupric chromites with an excess of cupric oxide above 900°, and

extracting the mass with nitric acid of sp. gr. 1·4. Cuprous chromite forms steel-blue or lead-grey triangular plates of sp. gr. 5·237. It is stable in oxygen above 875°, and in air above 770°. It does not oxidize in oxygen at a press. of 1087 mm. at 1020°. It is soluble in nitric acid of sp. gr. 1·4; but a mixture of nitric acid and potassium chlorate oxidizes the chromium to chromic acid. K. Fischbeck and E. Einecke prepared this salt and found that by cathodic polarization in 2 per cent. sulphuric acid, it is oxidized to chromate. L. and P. Wöhler and W. Plüddemann tried the salt as a catalytic agent for oxidizing sulphur dioxide.

J. F. Persoz obtained **cupric chromite,** $Cu(CrO_2)_2$, by heating to redness cupric chromate—L. and P. Wöhler worked above 870°—and extracting the product with hydrochloric acid; L. and P. Wöhler obtained it by heating the cuprous salt in oxygen below 870°, and extracting the mass with nitric acid; they precipitated mixed cupric and chromic hydroxides from a soln. of the mixed sulphates in eq. proportions by means of sodium carbonate, heated the washed product in oxygen at 700°, and then extracted it with dil. acids; C. H. Boehringer treated a soln. of basic cupric chloride with copper tetramminoxide; and M. Gerber heated to redness a mixture of cupric chloride and potassium dichromate, and washed the product first with boiling water, and then with hydrochloric acid. The bluish-black amorphous or crystalline product decomposes slowly at 1000°. If the compound be mixed with cupric oxide, and heated in vacuo, oxygen begins to be given off at 600°. The partial press. of the oxygen is 176 mm. at 779°; 440 mm. at 840°; and 795 mm. at 875°. At 850°, 38 Cals. are needed. The salt is not soluble in dil. acids, or in conc. hydrochloric acid; it is not attacked by sulphur dioxide; but it is oxidized by fused potassium nitrate. F. Wöhler and F. Mahla, and L. and P. Wöhler and W. Plüddemann studied its action as a catalyst in the oxidation of sulphur dioxide.

L. and P. Wöhler and co-workers obtained a basic salt, *cupric oxyoctochromite*, $CuO.4Cu(CrO_2)_2$, by heating commercial cupric chromate, in oxygen at 650°–700°, and extracting the mass with nitric acid. The black product decomposes at 1000°. M. Rosenfeld obtained *cupric trioxychromite*, $3CuO.Cu(CrO_2)_2$, by heating $6CuO.Cr_2O_3.CrO_3$; *cupric hexoxychromite*, $6CuO.Cu(CrO_2)_2$, by heating $7CuO.2CrO_3.5H_2O$; and *cupric tridecoxychromite*, $13CuO.Cu(CrO_2)_2$, by heating $7CuO.CrO_3.5H_2O$; and the acid salt, *cupric hexachromite*, $CuO.3Cr_2O_3$, by heating $CuCr_4O_9.Cr_2O_3.12H_2O$.

According to K. S. Nargund and H. E. Watson, mixtures of calcium and chromic oxides, when heated in vacuo, yield **calcium chromite,** $Ca(CrO_2)_2$; which when treated with acids, yields $CaO.2Cr_2O_3$. Z. Weyberg obtained the same product as prismatic, pleochroic, green needles by melting china clay with a large excess of potassium chromate and calcium oxide. M. Kreps obtained calcium chromite by adding ammonia to mixed soln. of calcium chloride and chrome-alum. F. de Carli said that the reaction between chromic oxide and calcium oxide begins at 550°. M. Gerber prepared calcium chromite by melting a mixture of mol. proportions of potassium dichromate and anhydrous calcium chloride, extracting the mass with water, and washing the product with boiling, conc. hydrochloric acid. E. Dufau obtained it by heating a mixture of chromic and calcium oxides in an electric furnace. K. Fischbeck and E. Einecke prepared this salt by direct sintering of the components. E. Dufau found that the dark olive-green product furnishes a crystalline powder, or pleochroic, prismatic needles, and it has a sp. gr. of 4·8 at 18°, and a hardness of 6. When heated in oxygen, it forms calcium chromate and chromic oxide; the oxidation begins below 100° in air; it is attacked by fluorine, or chlorine when warmed; hydrogen fluoride or chloride attacks it at a red-heat, but hydrofluoric or hydrochloric acid has no action, nor has sulphuric or nitric acid. It is decomposed by molten potassium carbonate, nitrate, or chlorate; Z. Weyberg added that it is slowly attacked by potassium hydrosulphate. T. J. Pelouze prepared **calcium oxychromite,** $CaO.Ca(CrO_2)_2$, by adding potassium hydroxide or ammonia to a mixture of a mol of chrome-alum and 2 mols of calcium chloride; H. Moissan obtained **calcium trioxychromite,** $3CaO.Ca(CrO_2)_2$, in yellow

plates, by heating chromium and calcium oxide in an electric furnace ; and E. Dufau, by heating a mixture of chromic and calcium oxides in the electric furnace. It might be added that the pottery colour, emerald green, is prepared by heating chromic oxide with a large proportion of calcium carbonate. A. Mitscherlich obtained **barium chromite,** $Ba(CrO_2)_2$, by heating a mixture of chromic and barium oxides to a white-heat. The crystals are soluble in hydrochloric acid ; and M. Gerber obtained it as a green crystalline powder by melting a mixture of anhydrous barium chloride and potassium dichromate, and washing the cold product with dil. hydrochloric acid. M. Kreps also prepared barium chromite by the action of ammonia on a soln. of chrome-alum and barium chloride. F. de Carli said that the reaction with chromic oxide and barium oxide begins at 220°. E. Dufau obtained **barium octochromite,** $BaO.4Cr_2O_3$, in black, hexagonal crystals of sp. gr. 5·4 at 15°, by heating a mixture of the two oxides in an electric arc-furnace. The product is stable. When heated in oxygen, it forms barium chromate and chromic oxide ; it is slowly attacked when heated with hydrogen fluoride or chloride ; acids are without action ; but it is easily attacked by fused alkali carbonate.

E. Mallard and J. J. Ebelmen melted together beryllium and chromic oxides in the presence of boric oxide, and obtained a dark green powder consisting of crystals of **beryllium chromite,** $Be(CrO_2)_2$. The crystals resemble alexandrite. The so-called *chrome spinel*, $(Mg,Fe)O.(Al,Cr)_2O_3$, from Lherz was called *lherzolite* by J. C. Delamétherie, but it was described earlier by P. Picot de la Peyrouse, and hence the name *picotite*. G. M. Bock, M. Websky, and A. Breithaupt described a related mineral which was called *magnochromite*, or *magnesiochromite—vide infra*, chromite. Analyses of picotite and magnesiochromite were reported by T. Thomson, B. Kosmann, F. Sandberger, A. Damour, A. Hilger, G. C. Hoffmann, C. Friedheim, and T. Petersen. E. S. Simpson proposed the term **picrochromite** —πικρός, bitter, in allusion to the bitter taste of magnesium salts—for members of the spinel-chromite series approaching in composition $Mg(CrO_2)_2$, discussed by T. S. Hunt, T. Petersen, E. Glasser, etc. There are four components, and the end-terms are : (1) *spinel*, $Mg(AlO_2)_2$—including spinel, ceylonite, and magnesiochromite ; (2) *hercynite*, $Fe(AlO_2)_2$—including hercynite and picotite ; (3) *picrochromite*, $Mg(CrO_2)_2$—including picrochromite and chromopicotite or magnesiochromite ; and (4) *chromite*, $Fe(CrO_2)_2$—including chromite, and beresofite. J. J. Ebelmen obtained **magnesium chromite,** $Mg(CrO_2)_2$, by melting a mixture of chromic and magnesium oxide with boric oxide in a porcelain oven, and extracting the product with hydrochloric acid. E. Schweitzer obtained it by calcining potassium magnesium chromate and extracting the residue with dil. and afterwards with hot conc. acid ; K. Fischbeck and E. Einecke, by the sintering of the components ; M. Gerber, by melting a mixture of anhydrous magnesium chloride and potassium dichromate, and extracting the product with hot conc. hydrochloric acid ; W. R. Nichols, by adding an excess of ammonia to a soln. of a mixture of a mol of magnesium sulphate and 1·19 mols of chrome-alum and some ammonium chloride—M. Kreps used a similar process—and E. Dufau, by heating in the electric arc-furnace a mixture of chromic and magnesium oxides. M. L. Huggins showed that the crystals are of the spinel type, and he discussed the electronic structure. S. Holgersson found that the X-radiogram gave for the lattice parameter $a=8·32$ A. and the sp. gr. 4·45 ; L. Passerini gave $a=8·29$ A., the sp. gr. 4·49, and the vol. of unit cell $569·72\times10^{-24}$ c.c. J. J. Ebelmen said that the dark green octahedra have a sp. gr. 4·415 at 15° and scratch glass but not quartz. E. Dufau gave 4·6 for the sp. gr. at 20°, and said that the hardness is greater than that of quartz. F. Beijerinck found that it is a good conductor of electricity ; but it is not magnetic. E. Dufau observed that the compound is not changed when strongly heated ; it is oxidized with difficulty by oxygen at a red-heat ; it is not attacked by chlorine or bromine ; it is attacked with difficulty by hydrofluoric or hydrochloric acid ; J. J. Ebelmen said that it is not attacked by conc. hydrochloric acid. E. Dufau, and E. Schweitzer found that it is easily attacked by hot, conc. sulphuric acid ; it is

not attacked by boiling nitric acid; it is insoluble in alkali-lye; and it is slowly attacked by molten potassium nitrate and chlorate—and, added W. R. Nichols, it is slowly oxidized to chromate by fused sodium carbonate and potassium nitrate. W. R. Nichols obtained **magnesium oxychromite,** $MgO.Mg(CrO_2)_2$, by adding an excess of ammonia to a mixed soln. of chrome-alum and an excess of magnesium sulphate. G. Viard obtained it as a pale brown powder, by calcining at a red-heat either magnesium chromate, or potassium magnesium chromate. When further heated it passes into **magnesium oxyoctochromite,** $MgO.4Mg(CrO_2)_2$; if potassium dichromate mixed with magnesium oxide be heated to redness, **magnesium oxytetrachromite,** $MgO.2Mg(CrO_2)_2$, is formed. According to M. R. Nayar and co-workers, magnesium chromate decomposes at 650°, forming chromites from which the magnesium oxyoctochromite, $MgO.4Mg(CrO_2)_2$, can be obtained as an insoluble residue after extraction with hydrochloric acid; a mixture of equimolar proportions of magnesia and chromic oxide above 600° yields **magnesium oxydecachromite,** $MgO.5Mg(CrO_2)_2$. W. R. Nichols prepared **magnesium tetrachromite,** $MgO.2Cr_2O_3$, by adding ammonia to a mixed soln. of a mol of magnesium sulphate and 2·02 mols of chrome-alum.

J. J. Ebelmen prepared **zinc chromite,** $Zn(CrO_2)_2$, by the method used for the magnesium salt; M. Gerber, by heating a mixture of anhydrous zinc chloride and an excess of potassium dichromate; G. Chancel, and M. Gröger, by adding potassium hydroxide to a mixed soln. of equimolar parts of a zinc and a chromic salt; and G. Viard, by passing the vapour of zinc chloride in a current of nitrogen or carbon dioxide over heated potassium chromate, and washing the mass with water, and conc. hydrochloric acid. K. Fischbeck and E. Einecke made it as in the case of the magnesium salt. M. L. Huggins showed that the crystals are of the spinel type and he discussed the electronic structure. According to J. J. Ebelmen, the black octahedral crystals have a sp. gr. 5·309, and they are harder than quartz. G. Viard gave 5·29 for the sp. gr. at 13°. L. Passerini calculated 4·436 for the sp. gr. from the lattice data; and found the lattice has the side $a=8·280$ A.; S. Holgersson gave $a=8·323$ A. W. Biltz and co-workers discussed the mol. vol. E. W. Flosdorf and G. B. Kistiakowsky examined a mixture of chromic and zinc oxides as a catalyst.

M. Gröger prepared violet-brown *zinc pentoxyhexachromite,* $5ZnO.3Zn(CrO_2)_2$, by heating potassium zinc chromate, and extracting the product with water; G. Viard obtained *zinc oxydichromite,* $ZnO.Zn(CrO_2)_2$, by calcining ammonium zinc chromate; *zinc oxytetrachromite,* $ZnO.2Zn(CrO_2)_2$, by calcining a mixture of zinc chloride and potassium chromate; and *zinc oxydecachromite,* $ZnO.5Zn(CrO_2)_2$, by calcining at a red-heat a mixture of zinc oxide and potassium dichromate.

G. Viard obtained **cadmium chromite,** by passing the vapour of cadmium chloride, in a current of nitrogen or carbon dioxide, over potassium chromate at a white-heat; also by heating cadmium chromate to dull redness, or likewise by heating a mixture of cadmium oxide and potassium dichromate. K. Fischbeck and E. Einecke made it as in the case of the magnesium salt. M. L. Huggins showed that the crystals are of the spinel type and he discussed the electronic structure. S. Holgersson gave $a=8·60$ A. for the lattice parameter, and 5·84 for the sp. gr. According to G. Viard, the black, octahedral crystals have a sp. gr. of 5·79 at 17°; they scratch glass but not quartz; and they are stable in acids.

L. Passerini found that chromic oxide forms a series of solid soln. when it is heated with alumina, but no **aluminium chromite** is formed; the lattice constants of the solid soln. range from $a=4·950$ A. for $Cr_2O_3$ to 4·740 A. for $Al_2O_3$, and $c=6·806$ A. to 6·478 A. S. Veil heated compressed mixtures of ceric and chromic oxides, and determined the electrical conductivities and coeff. of magnetization of the mixtures. The resulting curves indicated the existence of **ceric dichromite,** $CeO_2.Cr_2O_3$; **ceric tritoctochromite,** $3CeO_2.4Cr_2O_3$; **ceric tetrachromite,** $CeO_2.2Cr_2O_3$, or $Ce(CrO_2)_4$; and **ceric decachromite,** $CeO_2.5Cr_2O_3$; and the probable existence of **ceric pentitadichromite,** $5CeO_2.Cr_2O_3$; **ceric heptitoctochromite,** $7CeO_2.4Cr_2O_3$; and

**ceric octodecachromite,** $CeO_2.9Cr_2O_3$. G. Chancel mixed alkaline soln. of lead and chromic oxides, and obtained a green precipitate of **lead chromite,** $Pb(CrO_2)_2$. S. H. C. Briggs obtained **antimony oxychromite,** $2Sb_2O_3.Cr_2O_3$, by heating 3·5 grms. of antimony oxychloride, $2SbOCl.Sb_2O_3$, with 8 grms. of chromic trioxide and 8 c.c. of water in a sealed tube for 5 hrs. at 200°. The brown powder was thoroughly washed and dried. It was insoluble in alkali-lye, water, acids, and aqua regia. S. H. C. Briggs heated a mixture of 5 grms. of bismuth oxychloride, 6 grms. chromic trioxide, and 6 c.c. of water in a sealed tube at 200° for 5 hrs. The brown product, **bismuth oxychromite,** $3Bi_2O_3.2Cr_2O_3$, resembled antimony oxychromite. For **tungstic chromite,** *vide infra,* chromium tungstate. C. F. Rammelsberg obtained what was thought to be a yellowish-brown precipitate of **uranium chromite** mixed with chromate by treating uranium tetrachloride with potassium chromate.

J. J. Ebelmen obtained **manganese chromite,** $Mn(CrO_2)_2$ by heating a mixture of manganous and chromic oxides and boric oxide in a porcelain oven, and washing the product with hot, conc. hydrochloric acid. K. Fischbeck and E. Einecke made it as in the case of the magnesium salt. M. Gerber obtained it by melting a mixture of anhydrous manganese chloride and potassium dichromate. M. L. Huggins showed that the crystals are of the spinel type and he discussed the electronic structure. J. J. Ebelmen found that the iron-grey, octahedral crystals have a sp. gr. of 3·87. S. Holgersson gave for the space-lattice $a$=8·487 A. J. J. Ebelmen found that the crystals scratch glass ; they resist attack by acids, and are oxidized by molten potassium hydroxide and potassium nitrate—*vide infra,* manganese chromate.

The discovery of **ferrous chromite,** $Fe(CrO_2)_2$, or $FeO.Cr_2O_3$, by L. N. Vauquelin [2] has been previously discussed. The occurrence and some analyses of the mineral have also been indicated.

Analyses have been reported by H. Abich, E. Bechi, E. Berthier, G. M. Bock, J. C. Booth and C. Lea, L. H. Borgström, A. Christomanos, F. W. Clarke, E. Divers, L. Duparc and S. P. de Rubies, T. H. Garrett, A. Hilger, A. Hofmann, G. C. Hofmann, K. von John and C. F. Eichleitner, M. Z. Jovicic, E. Kaiser, A. Knop, F. Kovar, H. E. Kramm, A. Lacroix, A. Laugier, A. Liversidge, W. G. Maynard, G. P. Merrill, A. Moberg, H. Pemberton, T. Petersen, J. H. Pratt, G. T. Prior, C. F. Rammelsberg, L. E. Rivot, F. Ryba, H. Seybert, E. V. Shannon, E. S. Simpson, J. L. Smith, W. Tassin, H. Traube, G. Tschermak, F. W. Voit, T. Wada, W. Wallace and R. M. Clark, M. Websky, and A. E. V. Zeally.

The formula was discussed by C. F. Rammelsberg, P. Niggli, E. S. Simpson, N. Federowsky, and A. Lacroix. L. W. Fisher found that pure chromite has been found only in meteorites ; with other varieties there is a wide variation in the proportions of acid and base. Nearly all the chromites which have been analyzed show one or more oxides in excess. This may be due to incomplete separation of chromite and gangue. Consequently, its composition can seldom be represented by a definite formula. Chromite is a member of the spinel family, but all the family cannot be represented in definite isomorphous series.

The mineral was called *iron-chrome,* or rather *Eisenchrom* by P. Meder, and D. L. G. Karsten ; *siderchrom,* by J. J. N. Huot ; *chromoferrite,* by E. J. Chapman ; and **chromite,** by W. Haidinger. Although the composition approximates $Fe(CrO_2)_2$. the iron may be in part replaced by magnesium to form *magnochromite* or *magnesiochromite* (*q.v.*), specimens of which were described by A. Breithaupt, M. Websky, and G. M. Bock. Some of the chromium may be replaced by aluminium and by ferric iron as in the *chromopicotite* from the Dun Mt., New Zealand, described by T. Petersen. Chromite thus merges by gradations into spinel—*e.g. picotite.* A. Lacroix described a black mineral from Madagascar to which he gave the name *chromohercynite,* and its composition approximated $Fe(CrO_2)_2.(Fe,Mg,Mn)(AlO_2)_2$, and its sp. gr. 4·415. According to H. Arsandaux, the chromite of Mow Djeti, Togo, is a *chromiferous ferropicotite,* $(Mg,Fe,Mn)O.(Cr,Al,Fe)_2O_3$. The *mitchellite* of J. H. Pratt can be represented by $(Fe,Mg)O.(Cr,Al)_2O_3$. The mineral *chromitite*

obtained by M. Z. Jovicic from Western Siberia is possibly a mixture of chromite and magnetite. The incomplete analysis corresponds with $Fe_2O_3.Cr_2O_3$, but ferric and ferrous oxides are not distinguished in the analysis. The sp. gr. is 3·1. H. Forestier and G. Chaudron found that ferric and chromic oxides form solid soln.

The special occurrence of chromite was discussed by A. Arzruni, E. Berwerth, E. Cohen and E. Weinschenk, L. Colomba, J. S. Diller, C. Doelter, E. von Federoff and W. Nikitin, L. Cascuel, A. C. Gill, S. G. Gordon, H. S. Harger, R. Helmhacker, V. Hilber and I. Ippen, F. C. Hochstetter, C. Hütter, E. Kaiser, P. Kato, J. H. Lewis, A. Liversidge, L. F. Lubogetzky, R. W. E. MacIvor, H. B. Maufe and co-workers, M. P. Melnikoff, A. Michel-Lévy, J. H. Pratt, A. Rocati, B. Simmersbach, E. V. Shannon, A. Stella, O. Stutzer, P. A. Wagner, W. Wallace and R. M. Clark, O. Weiss, H. E. Williams, F. Zirkel, etc.—*vide supra*, the occurrence of chromium.

The origin of chromite was discussed by B. Baumgärtel, F. Beyschlag and co-workers, C. Camsell, A. Himmelbauer, A. de Launay, J. H. Pratt, F. Ryba, G. M. Schwartz, E. Sampson, L. W. Fisher, F. E. Keep, C. S. Ross, J. T. Singewald, J. H. L. Vogt, and P. A. Wagner. The occurrence of chromite in meteorites was described by E. Cohen, A. Daubrée, A. Eberhard, L. Fletcher, H. B von Foullon, W. Haidinger, O. W. Huntington, G. F. Kunz, A. Laugier, N. S. Maskelyne, C. F. Rammelsberg, G. Rose, C. U. Shepard, J. L. Smith, F. Stromeyer, G. Tschermak, T. N. Tschernyschoff, R. D. M. Veerbeck, V. Wartha, and F. Wöhler.

J. J. Ebelmen obtained black octahedral crystals by heating in a porcelain oven a mixture of chromic and ferric oxides, tartaric acid, and boric oxide; S. Meunier, by heating a mixture of iron filings, ferrous carbonate and potassium dichromate, or a mixture of alumina, colcothar, chromic oxide, and cryolite, or a mixture of chrome oxide, ferrous chloride, in a crucible lined with cryolite; and M. Gerber, by melting a mixture of anhydrous ferrous chloride and potassium dichromate. Chromite was also prepared by J. A. Hedvall, and K. Fischbeck and E. Einecke, by heating an intimate mixture of the component oxides; and by S. Meunier, by heating chlorides of iron and chromium in hydrogen, and afterwards in steam. J. H. Pratt found a peridotitic magma, containing an excess of magnesia, and a little aluminium and chromic oxides, in which crystals of chromite were present; and J. H. L. Vogt observed that chromite and picotite seem to separate first from such magmas. J. Clouet, and F. Fouqué and A. Michel-Lévy described crystals of a product with crystals like those of chromite, but with the composition **ferrous oxychromite,** $FeO.Fe(CrO_2)_2$; they were obtained by adding ammonia to a mixed soln. of iron and chromium sulphates, and heating the precipitate with borax. C. Sandonnini observed that no ferrite is formed when a mixture of ferrous and chromic hydroxides is oxidized.

Chromite commonly occurs in granular or compact masses of an iron-black or brownish-black colour, which, according to J. Thoulet, may be yellowish- or brownish-red when viewed by transmitted light in thin sections. Chromite also occurs in octahedral crystals described by E. Hussak. J. Königsberger proved that the crystals are isotropic. G. Sukkow found some crystals twinned according to the spinel law; and A. Knop observed some chromite crystals with growths of rutile and zircon. Ferrous and magnesium chromites form solid soln.; so also do ferrous chromite and ferrous aluminate. There is also evidence that some ferrites and chromites form solid soln. L. W. Fisher found that members of the spinel family are not always isomorphous, but that these series are so: (i) spinel, magnochromite, and chromite; (ii) magnetite, kreittonite, dysluite, and jahrite; (iii) spinel, magnesioferrite, and magnetite; and (iv) gahnite, spinel, and franklinite. P. F. Kerr studied the X-radiograms; and P. E. Wretblad, and L. Passerini found that ferric and chromic oxides furnish a complete series of solid soln. with cells having axial ratios and densities which are linear functions of the composition. The subject was discussed by G. Grenet. L. Tokody found that the cubic lattice of chromite has $a=8·05$ A., and eight mols. per unit lattice; and S. Holgersson gave

$a$=8·319 A. P. Niggli discussed the lattice structure which is taken to be that of the spinels—*vide* magnetite. H. Schneiderhöhn discussed the microstructure of polished sections of the mineral. L. W. Fisher said that the colour of these sections corresponds roughly with the chemical composition. With a low proportion of chromic oxide as in picotite, the colour is yellowish-brown; and with a high proportion of chromic oxide the colour is deep cherry-red or coffee-brown. Anastomosing black, opaque lines traversing translucent grains are due to the presence of a foreign substance present either as a solid soln., or deposited as a cement along narrow or incipient fractures. The sp. gr. of the mineral ranges from 4·1 to 4·9; E. F. Harroun and E. Wilson gave 3·88 to 4·15. J. J. Ebelmen's artificial chromite had a sp. gr. of 4·97—*vide infra*. The less the proportion of iron, the smaller the sp. gr., and the harder the mineral on the octahedral face. The hardness is about 5·5. P. J. Holmquist obtained the following results for the cutting hardness on the octahedral faces when the hardness of quartz is 1000. The hardnesses of the samples with an asterisk are mean values for all the faces.

| | | | | | | |
|---|---|---|---|---|---|---|
| Sp. gr. . . | 3·6 | 3·2 | 3·6 | 4·116 | 4·283 | 4·283 |
| Hardness . | 1779 | 1621 | 1531* | 1232* | 1031* | 806* |

The hardness decreases from that spinel proper, $Mg(AlO_2)_2$, as the proportion of iron and chromium increases. Y. Tadokoro found the coeff. of thermal expansion and sp. gr. of chromite bricks to be:

| | 20° | 100° | 250° | 500° | 750° | 950° |
|---|---|---|---|---|---|---|
| Sp. gr. . . | 2·982 | 2·978 | 2·966 | 2·945 | 2·925 | 2·910 |
| Coeff. expansion | — | $0{\cdot}0_570$ | $0{\cdot}0_597$ | $0{\cdot}0_590$ | $0{\cdot}0_588$ | $0{\cdot}0_590$ |

The thermal expansions of chromite from different sources, between 20° and 1000°, in oxidizing and reducing atm., were:

| | Oxidizing. | Reducing. |
|---|---|---|
| Rhodesian . . . . . | $7{\cdot}29\times10^{-6}$ | $17{\cdot}45\times10^{-6}$ |
| African . . . . . | $8{\cdot}51\times10^{-6}$ | $39{\cdot}01\times10^{-6}$ |
| Grecian . . . . . | $8{\cdot}32\times10^{-6}$ | $10{\cdot}06\times10^{-6}$ |
| Indian . . . . . | $7{\cdot}29\times10^{-6}$ | $15{\cdot}91\times10^{-6}$ |

F. H. Norton gave for the thermal conductivity:

| | 200° | 400° | 600° | 800° | 1000° | 1200° | 1400° |
|---|---|---|---|---|---|---|---|
| Heat conductivity . | 0·0034 | 0·0037 | 0·0039 | 0·0040 | 0·0040 | 0·0041 | 0·0041 |

H. Kopp found the sp. ht. of chromite to be 0·159 between 16° and 47°. E. D. Clark, and G. Spezia found that chromite fuses in the oxyhydrogen flame. A. Brun found samples of chromite with m.p., respectively, 1670° and 1850°. C. Doelter considered these results too high and gave 1450° for the m.p. of a sample from Kraubath and added that the mineral was liquid at 1600°. The m.p. of the mineral naturally depends on the proportion of iron, etc. E. S. Larsen found the index of refraction to be 2·08 to 2·10. W. W. Coblentz observed that the ultra-red reflecting power of chromite is uniformly 4 per cent. between wave-lengths 1$\mu$ and 11$\mu$. A. de Gramont studied the spark spectrum. W. T. Wherry found chromite to be a good radio-detector. T. W. Case said that chromite is a poor electrical conductor, and the conductivity is not affected by exposure to light. K. Fischbeck and E. Einecke found the resistance to be about $22\times10^4$ ohms. R. D. Harvey studied this subject. Chromite is not magnetic, but it may appear to be magnetic if contaminated with magnetite. E. F. Herroun and E. Wilson gave $79\times10^{-6}$ mass units for the magnetic susceptibility; and F. Stutzer and co-workers gave $244\times10^{-6}$ units for the coeff. of magnetization. H. A. J. Wilkens and H. B. C. Nitze discussed the magnetic separation of chromite. E. von Federoff observed pseudomorphs of hæmatite after chromite. According to E. Zalinsky, acids are without action on chromite; finely powdered magnetite was dissolved by hydrofluoric acid under conditions where chromite was not attacked. On the other hand, G. Piolti said that 200 c.c. of sulphuric acid, mixed with an equal vol. of water, dissolved 13·42 per cent. of chromite in about 56 hrs.; and a soln. of oxalic acid in the same

time formed a green soln. Y. Kato and R. Ikeno discussed the processes for decomposing chromite.

R. J. Elliot obtained dark green **cobalt chromite,** $Co(CrO_2)_2$, by precipitating a mixed soln. of equimolar parts of chrome-alum and cobalt chloride by sodium carbonate. The product is non-magnetic. G. Natta and L. Passerini obtained cobalt chromite and found that the length of unit cell of the spinel type is $a=8{\cdot}31$ A.; the vol. is $574\times10^{-24}$ c.c.; and the sp. gr. 5·14. J. A. Hedvall heated a mixture of cobalt and chromic oxides and obtained octahedral crystals of cobalt chromite which are but little attacked by acids. K. Fischbeck and E. Einecke prepared cobalt chromite by sintering a mixture of the component oxides; and similarly also with **nickel chromite,** $Ni(CrO_2)_2$. R. J. Elliot also obtained nickel chromite by a process analogous to that used for the cobalt salt. The greyish-green nickel chromite is non-magnetic. S. Veil found that the magnetization coeff. of mixtures of the constituent oxides show maxima corresponding with the pure chromites.

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## § 12. Intermediate Chromium Oxides

A number of oxides, with compositions intermediate between those of chromic oxide, $Cr_2O_3$, and chromic anhydride, $CrO_3$, has been reported. These oxides include $Cr_5O_9$, $Cr_3O_5$, $Cr_3O_6$, $Cr_5O_{13}$, $Cr_5O_{12}$, and $Cr_6O_{15}$. They are sometimes represented as *chromium chromates*. Their individuality is not well established. K. Honda heated chromium trioxide in an apparatus recording the losses in weight in terms of the movement of an indicator on a scale. There is first the expulsion of moisture, and, at about 300°, $Cr_6O_{15}$ is formed; then, at 420°, $Cr_5O_9$; and, at about 450°, chromic oxide, $Cr_2O_3$. The results agree with the magnetic observations of K. Honda and T. Sone,[1] who found that at about 280°, $Cr_6O_{15}$ is formed and at

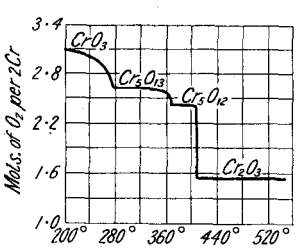


FIG. 22.—Losses in Weight on Heating Chromium Trioxide.

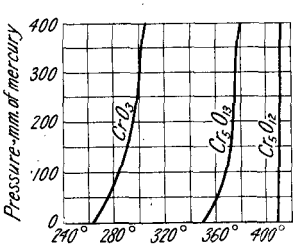


FIG. 23.—Dissociation Pressure Curves of the Chromium Oxides.

420°, $Cr_2O_3$; while between 300° and 400°, the strongly paramagnetic $Cr_6O_{15}$, and the ferromagnetic $Cr_5O_9$ are present as a mixture. A. Simon and T. Schmidt could not obtain these oxides. They observed only two intermediate oxides, as illustrated by Fig. 22, namely, **chromium pentitatridecoxide,** $Cr_5O_{13}$, and chromium pentitadodecoxide, $Cr_5O_{12}$. The other intermediate oxides reported in the literature either do not exist or are too unstable to appear under these conditions.

The first member, **chromium pentitenneaoxide,** $Cr_5O_9$, or $2Cr_2O_3.CrO_3$, was obtained by F. Wöhler by passing the vapour of chromyl chloride through a tube at a temp. between 300° and dull redness. If the temp. be too high, free chromic

oxide is formed; and A. Geuther and V. Merz said that if it be too low, free chromic anhydride will be present. A. Geuther and V. Merz also obtained a small yield of this oxide by heating chromic anhydride alone, or in a current of oxygen. According to O. Popp, an *enneahydrate*, $2Cr_2O_3.CrO_3.9H_2O$, is produced as a brown mass when a soln. of sodium thiosulphate, with potassium dichromate is boiled. E. Kopp said that this product is the $Cr_8O_{15}$-oxide. According to L. Blanc, if precipitated chromic oxide, $\alpha$-$Cr_2O_3$, be heated to 230° for some time it passes into chromium dioxide, $CrO_2$, and if this product be hydrolyzed, it forms amorphous or $\alpha$-$Cr_5O_9$; and if this product be heated between 350° and 400°, it forms a mixture of crystalline or $\beta$-$Cr_5O_9$, and $\beta$-$Cr_2O_3$. At 450°, this reaction is instantaneous with the evolution of much heat. At 300°, the reaction $2\alpha$-$Cr_5O_9+O_2 \rightarrow 10CrO_2$ occurs; and at 350°, $10CrO_2 \rightarrow 2Cr_5O_9+O_2$. According to L. Blanc, if a salt of tervalent aluminium, iron, or chromium be added to a soln. of a neutral chromate, and the precipitate be washed with boiling water, yellow aluminium chromate, $2Al_2O_3.CrO_3$; or brown ferric chromate, $2Fe_2O_3.CrO_3$; or brown chromic chromate, $2Cr_2O_3.CrO_3$, is formed as the case may be. It is therefore inferred that the pentita-enneaoxide is a chromic chromate. L. Blanc and G. Chaudron assumed that there are two forms of $Cr_5O_9$ with a transition temp. at 440°—*vide supra*, chromic oxide. A. Geuther and V. Merz observed that the $Cr_5O_9$-oxide furnishes rhombic prisms paler in colour than chromic oxide, and having a violet tinge. The sp. gr. is 4·0 at 10°; and they considered that F. Wöhler's amorphous, black powder was probably the impure oxide. F. Wöhler said that the compound is magnetic, but, added E. Wedekind and K. Fetzer, not so magnetic as manganese phosphide. While F. Wöhler thought the magnetic oxide of chromium is $Cr_3O_4$; A. Geuther and V. Merz, $Cr_5O_9$; and I. Schukoff, $Cr_4O_9$, L. Blanc showed that the magnetic oxide is probably an unstable variety of $Cr_5O_9$ intermediate between the $\alpha$- and $\beta$-forms. The magnetic susceptibility with between 0 and 200 gauss is nearly equal to that of magnetite. K. Honda and T. Sone gave for the magnetic susceptibility, $\chi$, with a field of strength $H$ gauss:

| $H$ | 294 | 646 | 1306 | 2012 | 3064 | 6682 | 9260 |
|---|---|---|---|---|---|---|---|
| $\chi$ | 718 | 640 | 487 | 408 | 300 | 137 | 99 |

According to I. Schukoff, the intermediate oxides obtained by heating chromyl chloride or chromic anhydride are magnetic or not, according to the conditions. If the decomposition is controlled so that the temp. does not rise above 500°, the oxides obtained are only feebly magnetic. On heating, however, to 500°–510°, 13–14 per cent. of oxygen is evolved, and the black mass, which has the composition $2CrO_3.Cr_2O_3$, is strongly magnetic. An oxide of the same composition, but prepared at 450°, was very feebly magnetic. A crystalline magnetic oxide was obtained by the decomposition of chromyl chloride; when ignited, it loses only 3·4–4 per cent. of oxygen. According to F. Wöhler, the $Cr_5O_9$-oxide is reduced to chromic oxide when heated in hydrogen; and when heated in air, it forms green chromic oxide, and is then no longer magnetic. A. Geuther and V. Merz also found that the oxide is slowly reduced to chromic oxide when heated in air; it is insoluble in hydrochloric and nitric acids, in aqua regia, and in a mixture of nitric and hydrofluoric acids; boiling alkali-lye slowly decomposes it into chromic oxide and chromic anhydride; and it is easily decomposed by fused alkali hydroxides.

According to M. Traube,[2] when chromic anhydride is exposed on a glass plate, it dries to a brown crust which is insoluble in water, and adheres strongly to the glass. Its composition agrees with **chromium octitapentadecaoxide**, $Cr_8O_{15}$, or $2Cr_2O_3.3CrO_3$; and it is supposed to be produced by the action of the dust in the air. It can be obtained by treating a moderately dil. soln. of chromic acid at ordinary temp. with an excess of alcohol, and heating the mixture after the evolution of aldehyde has ceased. Part of the oxide settles quickly and part remains in suspension for some weeks. The precipitate is boiled until the smell of acetic is evident, then agitated with water, and lastly with alcohol until nothing is dissolved out by either liquid. The dried product is a greenish-brown

powder; before drying, the product is readily dissolved in hydrochloric and nitric acids, and alkali-lye, but less readily in acetic acid. Ammonia precipitates hydrated chromic oxide from the soln. in acids. A. Simon and T. Schmidt observed that when $Cr_8O_{15}.nH_2O$ is heated, water and oxygen are simultaneously given off between 100° and 400°. The brown powder obtained by C. F. Rammelsberg by mixing soln. of chrome-alum and potassium dichromate was considered to be the *enneahydrate*, $2Cr_2O_3.3CrO_3.9H_2O$; but C. W. Eliot and F. H. Storer showed that it is probably a mixture.

L. N. Vauquelin [3] prepared brown oxide of chromium, or **chromium dioxide,** $Cr_2O_3.CrO_3$, or $Cr_2O_4$, or $CrO_2$, or *chromyl chromate*, $(CrO)_2CrO_4$, by heating chromic nitrate until all the nitric acid is expelled, repeating the treatment with nitric acid, and finally heating the product short of redness; F. Brandenburg employed a similar process. M. Z. Jovitschitsch heated the nitrate to 290°; and L. Blanc heated amorphous chromic oxide to 280°—*vide supra*. A. Maus added that the temp. required to expel all the nitric acid results in the formation of chromic oxide. The product obtained by heating hydrated chromic oxide below redness, in air—to 200°–250°, according to H. Löwel—is, according to M. Krüger, chromium dioxide but C. W. Eliot and F. H. Storer, and M. Siewert said that this product is only a mixture. H. Moissan, and W. Manchot prepared this oxide by heating hydrated chromic oxide to 330°–440° in a current of oxygen; M. Z. Jovitschitsch said that anhydrous chromium chromate cannot be prepared by heating the hydrated oxide since decomposition occurs before the last mol. of water is expelled. G. N. Ridley obtained it by heating chromic anhydride to 250°; by passing sulphur dioxide over heated chromic anhydride; and by gently heating a mixture of chromic anhydride and phosphorus in a crucible until all takes fire. E. Moles and F. Gonzalez prepared the dioxide by heating ammonium dichromate to 225°; and E. Maumené, by heating ammonium chromate to 204°.

A number of hydrates of chromium dioxide has been reported. According to C. W. Eliot and F. H. Storer, the compound is not produced by boiling an aq. soln. of ammonium chromate; nor as indicated by L. N. Vauquelin, and H. Moser, by passing chlorine through a soln. of a chromic salt, and precipitating with potash-lye; nor, as indicated by H. Schiff, by treating hydrated chromic oxide, or violet chromic chloride with bleaching powder. K. Seubert and J. Carstens assumed that chromium dioxide is formed as an intermediate stage in the reduction of chromic anhydride by an iodide, or by hydrazine; but R. Luther and T. F. Rutter preferred the assumption that the reduction proceeds through stages involving sexi-, quinque-, quadri-, and ter-valent chromium. The reaction was also discussed by W. L. Miller. According to A. Maus, hydrated chromium dioxide is formed by digesting hydrated chromic oxide with a soln. of chromic acid—not in excess. A. Maus obtained it by digesting a hot soln. of potassium chromate with chromic chloride, A. Bensch, with chromic sulphate, and C. W. Eliot and F. H. Storer, with chrome-alum. E. Schweitzer, P. Grouvelle, and C. W. Eliot and F. H. Storer treated a soln. of potassium dichromate with nitric oxide; O. Popp, and E. Kopp, with sodium thiosulphate; G. N. Ridley, with stannous chloride; A. Vogel, and L. Godefroy, with alcohol; J. W. Swan, with organic substances; and H. Schiff, with oxalic acid. T. E. Thorpe obtained it by treating a soln. of chromium hexoxydichloride with ammonia. P. A. Meerburg found that colloidal chromium dioxide is formed when a soln. of chromic acid is treated with potassium iodide. The colloid is slowly modified with a decreased absorptive power. The amount of water absorbed over conc. sulphuric acid at ordinary temp. is greater than at 100°. A rise of temp. over 100° increases the loss of water, and decreases the absorptive power.

According to A. Vogel, the product dried at 100° is the *dihydrate*, $CrO_2.2H_2O$, while L. Godefroy represented it as a *hemitrihydrate*, $CrO_2.1\frac{1}{2}H_2O$, which he symbolized $(HO)_3{\equiv}Cr{-}O{-}Cr{\equiv}(OH)_3$. W. M. Horton found that by heating ammonium dichromate in air below 190° a *hemihydrate*, $2CrO_2.H_2O$, is formed as a black powder. J. J. Berzelius supposed the brown oxide prepared by L. N. Vauquelin to be a definite oxide; T. Thomson, and J. M. Godon de St.

Menin seem to have regarded it as a mixture of chromic oxide and chromic anhydride; and J. F. John, C. W. Eliot and F. H. Storer, J. W. Döbereiner, and A. Maus, as a feeble compound of green chromic oxide and chromic acid—namely, chromium chromate. According to M. Z. Jovitschitsch, when a soln. of chromic oxide in nitric acid is evaporated until excess of acid is removed and the residue is dissolved in water and treated with ammonia, a dark brown, almost black product is obtained, analyses of which are in agreement with the formula, $Cr_2(OH)_8.H_2O$, or $CrO_3.Cr_2O_3.7H_2O$. The loss of $1H_2O$ over sulphuric acid, of $2H_2O$ at 105°, and of $6H_2O$ at 205° is more readily explained by the former, but the chromium content and particularly the possibility of the preparation of anhydrous chromium chromate from the substance, favour the formula $Cr_2O_3.CrO_3.7H_2O$. The analytical data agree equally well with those required for the peroxide, $CrO_2$, but the readiness with which the substance is converted by ammonia, alkali carbonate, or hydroxide or by boiling water into chromium hydroxide and chromate is interpreted in favour of a salt-like constitution. W. Manchot and R. Kraus said that the product obtained by heating chromic hydroxide to 320° to 345° for several hrs. is a hygroscopic, black powder containing 6 to 7 per cent. of water. Its general properties are those of a peroxide and not of a chromic chromate, and the formula is probably O : Cr : O. It thus differs from the peroxide, O : Cr.O.O.Cr : O, which appears as the primary product of the autoxidation of chromous oxide. The existence of this chromium dioxide is regarded as evidence in favour of the view that chromium is quadrivalent in chromium trioxide. A. Simon and T. Schmidt observed that oxygen is given off, and the dioxide passes into chromic oxide at 380°. E. Moles and F. Gonzalez gave for the magnetic susceptibility $42{\cdot}2\times10^{-6}$ units.

Chromium dioxide is a dark grey, almost black, solid which gives off oxygen at 300° forming green chromic oxide. L. and P. Wöhler said that the decomposition of chromium dioxide in vacuo begins at about 280°. When prepared by igniting hydrated chromic oxide, W. Manchot and R. Kraus found that it contained 6 or 7 per cent. of water which is evolved along with oxygen at a red-heat, and chromic oxide remains. E. Hintz found that when heated with **chlorine,** at about 250°, it forms chromic and chromyl chlorides; when treated with **water,** it forms no chromic acid; but M. Martinon found that with **hydrogen dioxide,** oxygen is rapidly evolved at 68°, and the addition of a few drops of sulphuric acid results in the formation of blue perchromic acid. This agrees with the hypothesis that the dioxide is chromium chromate. H. Moissan, and W. Manchot and R. Kraus found that it reacts slowly with **hydrochloric acid** liberating chlorine; and it likewise reacts with **hydriodic acid** liberating iodine. M. Krüger said that with a mixture of pyrosulphuric acid and **sodium chloride,** chlorine and not chromyl chloride is formed; and with conc. sulphuric acid and sodium chloride, C. W. Eliot and F. H. Storer obtained chromyl chloride. H. Moissan, O. Popp, etc., found that it is soluble in **sulphuric acid.** W. Manchot and R. Kraus found that when warmed with **sulphur dioxide,** sulphur trioxide is formed; and warm **sulphurous acid** is converted into sulphuric acid. C. W. Eliot and F. H. Storer, O. Popp, etc., observed that chromic dioxide readily dissolves in dil. **nitric acid;** the soln. is reddish-brown, and gives a dirty green precipitate with ammonia. W. Manchot and R. Kraus found that conc. nitric acid converts the dioxide into chromic acid. E. Hintz found that it is scarcely attacked by **phosphorus pentachloride** at 250°. A. Maus stated that a little **arsenic acid** converts the dioxide into chromic arsenate, which is soluble in an excess of arsenic acid. The dioxide is insoluble in **ether, acetone,** and other organic liquids; and O. Popp said that the dioxide dissolves with difficulty in **acetic acid.** M. Krüger, W. Manchot and R. Kraus, etc., observed that boiling **potassium** or **sodium hydroxide** converts the dioxide into a soln. of alkali chromate, and a precipitate of hydrated chromic oxide. This simultaneous oxidation and reduction furnishes an illustration of the acidic and basic properties of chromium dioxide. A. Maus found that when digested with **lead acetate** in

the presence of acetic acid, lead chromate and chromic acetate are formed. E. Maumené said that the brown oxide is soluble in aq. **chromic acid,** or in soln. of **alkali dichromates,** and when the brown soln. are diluted with water, the brown oxide is re-precipitated.

I. Schukoff [4] heated chromic anhydride to 500°–510° and obtained *chromium tetritaenneaoxide*, $Cr_4O_9$, or $Cr_2O_3.2CrO_3$. The magnetic qualities of this substance disappear at 120°–130°, and reappear on cooling. For $Cr_2O_3.6CrO_3$, *vide infra*, chromium dichromate. For **chromium pentitatridecoxide,** $Cr_5O_{13}$, *vide supra*. The heating curve of A. Simon and T. Schmidt is shown in Fig. 22, and the dissociation press. in Fig. 23. According to J. W. Döbereiner, and M. Traube, **chromium pentitadodecoxide,** $Cr_5O_{12}$, or $Cr_2O_3.3CrO_3$, *i.e.* normal *chromium chromate*, or *chromic chromate*, $Cr_2(CrO_4)_3$, is formed when chromic anhydride is heated to about 250°. By boiling the product with water, or after standing a long time in contact with that liquid, it is converted into a soluble modification. The other reactions resemble those obtained with the preceding oxide. A. Simon and T. Schmidt's heating curve is shown in Fig. 22, and the dissociation press. curve in Fig. 23. G. Rothaug's observations were discussed in connection with the oxidation of chromic oxide. S. Takegami observed that chromic chromate is sometimes deposited in a colloidal form on the cathode during the electrolysis of soln. of chromic acid. This occurs when the ratio of ter- to sexivalent chromium is 1 : 0·5. Observations were previously made by E. Müller and co-workers who regard the film as $Cr_2(OH)_4CrO_4$—*vide supra*, the deposition of chromium. A. Maus found that *chromium hexitapentadecaoxide*, $Cr_6O_{15}$, or $Cr_2O_3.4CrO_3$, is formed when a hydrated chromic oxide or chromic carbonate is dissolved in a cold, aq. soln. of chromic acid, and the soln. evaporated. The brittle, horny product is permanent in air, and dissolves without change in alcohol ; the soln. may be evaporated a number of times at 100° without decomposition, but A. A. Hayes observed that if kept for a long time at that temp. the compound becomes insoluble. K. Honda and co-workers obtained this product by heating chromium trioxide to 280°, and they said that its magnetic susceptibility at room temp. is $14{\cdot}2\times10^{-6}$. C. D. Braun treated a conc. aq. soln. of potassium ferrocyanide with potassium dichromate, and on evaporation obtained a resinous mass of the *dodecahydrate*, $Cr_6O_{15}.12H_2O$.

C. W. Eliot and F. H. Storer summed up the result of their examination of these intermediate oxides by saying : "There is not a particle of evidence of the existence of any chromate of chromium containing more than one equivalent of chromic acid." The position is very nearly the same to-day.

According to J. Heintze,[5] by passing a slow current of ammonia into a dil. chloroform soln. of chromyl chloride and by evaporating the solvent, there remains brown **ammonium chromochromate,** $NH_4O.CrO_2.O.Cr.O.CrO_2.ONH_4$, which loses water and ammonia when heated, forming chromic oxide. The salt forms a brownish-yellow soln. with water, but it is insoluble in alcohol, ether, chloroform, and glacial acetic acid ; it dissolves in conc. acids, and the acid soln., when diluted with water, deposits the original salt as a brown powder. The salt is decomposed by soda-lye, giving off ammonia. J. Heintze prepared **potassium chromochromate** in an analogous manner, but neither A. Leist, nor A. Werner and A. Klein could verify this. D. Tommasi reported **potassium chromic hydroxychromate,** $K_2CrO_4.2Cr(OH)CrO_4$, to be formed by the action of nitric oxide on a soln. of one part of potassium dichromate in 2 parts of fuming nitric acid, at 70° ; evaporating the product to dryness on a water-bath ; extracting with hot water ; and drying at 150°. The violet-brown, amorphous powder is without taste or smell ; its sp. gr. at 14° is 2·28 ; it melts at 300°, and decomposes : $K_2CrO_4.2Cr(OH)CrO_4 = 2Cr_2O_3+K_2CrO_4+H_2O+3O$. When mixed with potassium chlorate it does not detonate by percussion, but it burns vigorously when heated. It is insoluble in water, alcohol, and acetic acid ; conc. nitric acid has very little action in the cold, but when heated the salt is partially oxidized. The salt is not attacked by cold, conc. sulphuric acid, but the hot acid forms a green soln. ; and with hot, conc. hydrochloric acid, chlorine is evolved.

DropBooks

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## § 13. Chromium Trioxide, and Chromic Acid

The oxidation of chromic oxide, or hydrated chromic oxide furnishes **chromium trioxide,** or **chromic anhydride,** $CrO_3$; it was discovered by A. Mussin-Puschkin,[1] and afterwards investigated by L. N. Vauquelin, H. Moser, and J. B. Richter. Chromic oxide is oxidized to chromium trioxide, as previously indicated, by heating it in the presence of bases in air. J. Milbauer found that with oxygen at 12 atm. press., and 300°, only a partial conversion of chromic oxide to chromium trioxide occurs; and the conversion is complete at 460° and 12 atm. press. in the presence of the oxides of silver, magnesium, zinc, cadmium, and lead. The oxidation occurs more readily than with oxygen if chromic oxide be heated with oxidizing agents—*e.g.* alkali nitrate, chlorate, dioxide, etc. A. Mailfert found that ozone converts chromic hydroxide into chromium trioxide. In alkaline soln., chromic oxide or hydroxide is oxidized to the trioxide by chlorine or hypochlorite (A. J. Balard,

H. Vohl), fluorine (F. Fichter and E. Brunner), bromine (F. H. Storer, F. Melde), iodine (E. Lenssen), hydrogen dioxide or alkali dioxide (E. Lenssen), potassium persulphate (H. Marshall, and D. M. Yost), potassium ferricyanide (E. Lenssen), potassium permanganate (A. Reynoso, S. Cloez and E. Guignet, and E. Bohlig), perchloric acid (J. J. Lichtin), lead dioxide (G. Chancel), manganese dioxide (F. H. Storer), mercuric oxide (F. H. Storer), copper oxide (O. W. Gibbs), and silver oxide (D. Meneghini). In acidic soln., according to F. H. Storer, A. Terni, and M. Salinger, chromic oxide is oxidized by potassium permanganate, or by lead or manganese dioxide; and, according to M. Holzmann, by ceric nitrate. O. Stumm found that chromic salts in alkaline soln. can be oxidized by molecular oxygen, using manganese hydroxide, copper hydroxide, cerium hydroxide, silver oxide and iodide, and amalgamated copper as catalytic agents. For the electrolytic oxidation, *vide supra*, the extraction of chromium.

K. Fischbeck and E. Einecke found that the cathodic polarization of ferrous, cuprous, calcium, and magnesium chromites produces chromic acid, whilst the other chromites are unaffected, and natural chrome ironstone behaves in a like manner, but other commercial chromites are reduced on cathodic polarization, and yield chromic acid on anodic polarization. Chromites behave as an intermediate electrode. O. Unverdorben observed that chromyl fluoride, prepared by heating a mixture of fluorspar, lead chromate, and sulphuric acid, when passed into water, furnishes an aq. soln. of this oxide. The soln. was treated with silver nitrate, and the washed precipitate of silver chromate decomposed by hydrochloric acid. A. Maus said that anhydrous sulphuric acid or fuming sulphuric acid is not suited for the preparation because of its volatilization with the chromyl fluoride. J. J. Berzelius employed a somewhat similar process using either lead or barium chromate. A. Maus treated a hot soln. of potassium dichromate with insufficient hydrofluosilicic acid to precipitate all the potassium; the filtered soln. was evaporated and again treated with hydrofluosilicic acid, and evaporated to dryness in a platinum dish. The residue was taken up with a little water, filtered, and evaporated for chromic anhydride. D. G. Fitzgerald and B. C. Molloy precipitated the potassium as potash-alum by adding aluminium sulphate, and removed the sulphuric acid by ignition. J. Fritzsche added a warm soln. of potassium dichromate to an excess of conc. sulphuric acid; the chromic anhydride separates in small red crystals. The liquid is drained from the crystals, which are then dried on a porous tile over sulphuric acid. The crystals are then recrystallized from an aq. soln. P. A. Bolley said that the chromic anhydride so prepared contains a little sulphuric acid as impurity and the Metals Protection Corporation removed the sulphate by means of barium hydroxide, carbonate, or chromate. R. Bunsen, A. V. Rakowsky, A. Dalzell, F. Dietze, O. Ficinus, H. Moissan, A. Schafarik, M. Traube, J. Voisin, G. Vulpius, R. Warington, and E. Zettnow employed modifications of these processes.

G. P. Baxter and co-workers purified chromium trioxide suitable for at. wt. determinations by repeated filtration, and recrystallization from aq. soln. M. Siewert treated barium chromate with nitric acid, crystallized out the barium nitrate; removed the nitric acid by evaporation to dryness; and recrystallized the product. E. Duvillier used a similar process, and afterwards substituted lead chromate for barium chromate. K. F. W. Meissner, F. Kuhlmann, J. W. Döbereiner, and W. A. Rowell treated barium chromate with sulphuric acid; and A. Schrötter, lead chromate. The filtered liquid in each case was evaporated for crystallization. J. Thomsen, and J. Krutwig similarly treated silver chromate with hydrochloric acid. A. Mailfert found that chromium trioxide is formed when soln. of chromic salts or chromic oxide are treated with ozone. M. Prud'homme and F. Binder observed that if barium chloride is added to a soln. of barium dichromate, normal barium chromate is precipitated, and potassium chloride and chromic acid remain in soln. In preparing chromic acid, V. V. Polyansky first obtained calcium chromate by addition of calcium hydroxide paste, followed by calcium chloride soln., to

aqueous sodium dichromate; the mixture is concentrated on the water-bath, the precipitate of calcium chromate being collected and dried. Two parts of the aq. soln. is treated with one part of sulphuric acid (sp. gr. 1·84), kept on the water-bath, decanted, and this procedure repeated until no more calcium sulphate is precipitated, when chromic anhydride is crystallized. The product is treated with nitric acid (sp. gr. 1·4), and dried at 60°–100°.

For the electrolytic oxidation of soln. of chromic salts to chromic acid or the chromates, *vide supra*. According to E. Müller and M. Soller, a soln. of chrome-alum in $N$-$H_2SO_4$ is not appreciably oxidized to chromic acid with a smooth platinum anode, but when traces of a lead salt are present in the soln., lead dioxide is deposited on the anode, and oxidation then occurs. About one-third of the oxidation which occurs with a lead dioxide anode occurs when an anode of platinized platinum is used. With a lead dioxide anode, the oxidation occurs quantitatively in fairly conc. soln. of chrome-alum, when the current density is not too high—about 0·005 amp. per sq. cm. is suitable. The difference in the results is not due to the lead dioxide anode having a higher potential than the platinum anode, since the reverse is rather the case. The effect is attributed to the catalytic action of lead dioxide which oxidizes the chrome-alum chemically. P. Askenasy and A. Révai showed that in regenerating soln. of chromic sulphate, at first, when the conc. of the chromic acid is small, it is better to use low-current densities at the cathode, and to increase the current density as the conc. of chromic acid increases. Temp. has little influence on the process. The addition of magnesium sulphate prevents a reduction at the cathode when dil. soln. and low current densities are employed, but if there is only a small percentage of chromic acid present it has the opposite effect, and if high current densities are used, it has no effect. The influence of chromium sulphate is to prevent reduction with both high and low-current densities except in soln. which contain very little chromic acid. The addition of sodium and potassium sulphates is without influence on the reaction. Dilution is favourable to the oxidation under all circumstances, but more especially with high-current densities and in the presence of magnesium sulphate when low-current densities are employed. A high conc. of sulphuric acid has a slightly favourable action. A. R. y Miro found that the presence of potassium fluoride favours the electrolytic oxidation of chrome-alum to potassium dichromate.

It is doubtful if hydrated chromium trioxide has been prepared in the solid state. H. Moissan [2] said that if an almost sat. aq. soln. of chromium trioxide be kept for several hrs. at about 90°, and then cooled below 0°, small red crystals of **chromic acid,** $H_2CrO_4$, collect on the walls of the containing vessel. This does not agree with J. J. Berzelius's observations, while F. Mylius and R. Funk, T. Costa, and E. Field were unable to confirm H. Moissan's observation. H. C. Jones showed that the f.p. of aq. soln. of chromium trioxide agreed with the assumption that the solvation for soln. with $m$ mols of $CrO_3$ per litre, can be represented by the mols of water in combination with a mol of $CrO_3$:

| | | | | | | |
|---|---|---|---|---|---|---|
| Mols $CrO_3$ per litre | 0·10 | 0·50 | 1·00 | 2·00 | 3·00 | 4·00 |
| Mols $H_2O$ per mol $CrO_3$ | 27·8 | 20·6 | 19·17 | 13·95 | 11·65 | 10·41 |

The crystals are chromium trioxide, $CrO_3$, not chromic acid, $H_2CrO_4$. The **solubility** of chromium trioxide in water was measured by R. Kremann who found that sat. soln. at $\theta°$ contained $S$ grms. of $CrO_3$ per 100 grms. of soln.

| | −74·0° | −64·0° | −52·0° | −43·0° | −28·3° | −16·3° | −2·0° |
|---|---|---|---|---|---|---|---|
| $S$ | 55·00 | 54·00 | 52·00 | 49·10 | 40·80 | 30·20 | 8·00 |

There is a eutectic at −105° with 57·2 per cent. of $CrO_3$. E. H. Büchner and A. Prins gave −155·0° for the eutectic with 60·5 per cent. of $CrO_3$. At higher temp. J. Koppel and R. Blumenthal, F. Mylius and R. Funk, and R. Kremann found:

| | 0° | 15° | 30° | 50° | 82° | 100·0° | 127·0° |
|---|---|---|---|---|---|---|---|
| $S$ | 61·82 | 62·40 | 62·52 | 64·60 | 66·00 | 67·40 | 71·20 |

The results of E. H. Büchner and A. Prins are plotted in Fig. 24; there is no sign of the formation of a definite hydrate. C. F. Hüttig and B. Kurre also failed to find any evidence of the formation of any definite hydrate. Analyses of chromium trioxide by L. N. Vauquelin, S. M. Godon de St. Menin, C. F. Rammelsberg, J. J. Berzelius, and A. Schrötter are in agreement with the empirical formula $CrO_3$. W. Ostwald's observations on the electrical conductivity, and the lowering of the f.p. indicate that the **molecular weight** in aq. soln. of chromium trioxide corresponds with **dichromic acid,** $H_2Cr_2O_7$; and this is in agreement with a comparison of the absorption spectra of aq. soln. of chromium trioxide and potassium dichromate, for H. Settegast found these spectra are very much alike. According to R. Abegg and A. J. Cox, the electrical conductivity and f.p. of soln. of the dichromates agree with the assumption that dichromic acid, $H_2Cr_2O_7$, chromic acid, $H_2CrO_4$, and chromium trioxide are present. E. Spitalsky, however, interpreted the results of his observations on the ionization of the aq. soln. to mean that the soln. is ionized $H_2Cr_2O_7 \rightleftharpoons 2H^{\cdot} + Cr_2O_7''$. The resolution of the dichromate into chromate ions was not observed with a mol of $CrO_3$ in 5800 litres. E. Field's observations on the raising of the b.p. of aq. soln. indicate a mol. wt. of 171·85 when $H_2CrO_4$ requires 118·4, and $H_2Cr_2O_7$ requires 218·8. T. Costa's ebulliscopic measurements show that soln. which are not too concentrated, at 100° contain $H_2Cr_2O_7$, not $H_2CrO_4$; and that a soln. of chromic acid has the same electrical conductivity when cooled to 0° either directly or after heating to 100°, so that no chromic acid, $H_2CrO_4$, is formed in soln. K. Seubert and J. Carstens explained the action of hydrazine on the assumption that the soln. contained $H_2Cr_2O_7$, or $Cr_2O_7''$-ions. M. S. Sherrill found that the f.p. of soln. of ammonium chromate agreed with the assumption that $HCrO_4'$-ions are present. W. V. Bhagwat and N. R. Dhar, N. R. Dhar, and F. Auerbach assumed the existence of $H_2CrO_4$ in aq. soln. H. Lessheim and co-workers, and P. Niggli discussed the electronic structure.

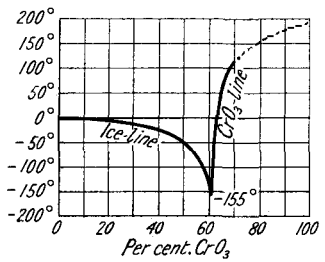
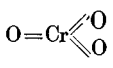
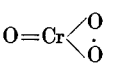



FIG. 24.—Solubility Curve of Chromium Trioxide.

The generally accepted view—*vide supra*—is that chromium is sexivalent in the trioxide; but W. Manchot supposed that it is quadrivalent:

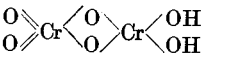



Sexivalent Cr

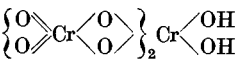



Quadrivalent Cr

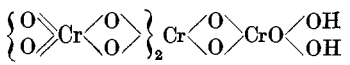
he supported this hypothesis by comparing the reactions of the trioxide with those of the peroxides, but R. Luther and T. F. Rutter did not agree. A. Geuther supposed that the polychromates are salts of hypothetical polychromic acids:




Dichromic acid.

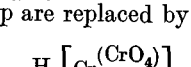



Trichromic acid.

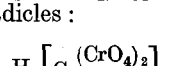



Tetrachromic acid.

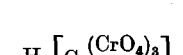
A. Miolati represented chromic acid on the co-ordination theory by $H_2[CrO_4]$, and the polychromic acids by $H_2[Cr(CrO_4)O_3]$, in which the oxygen atoms of the $O_3$-group are replaced by $CrO_4$-radicles:




Dichromate, $-H_2Cr_2O_7$.




Trichromate, $-H_2Cr_3O_{10}$.




Tetrachromate, $-H_2Cr_4O_{13}$.

In addition to a number of inorganic polychromates, R. Weinland and H. Staelin prepared dichromates of quinoline and guanidine; and trichromates of quinoline, pyridine and guanidine. A. Werner represented dichromic acid as a derivative

of dimolecular chromium trioxide $(CrO_3)_2$, and on his co-ordination theory, dichromic acid becomes:

$$\left[\begin{matrix} O & & O \\ OCr & \ldots & OCr \ldots O \\ O & & O \end{matrix}\right] H_2$$

**The physical properties of chromium trioxide.**—The evaporation of the aq. soln. of chromium trioxide furnishes a dark red mass. The colour was found by F. Rinne [3] to darken with a rise of temp., and to be restored on cooling. When the trioxide is crystallized in the presence of sulphuric acid, dark red, needle-like **crystals** are formed, which, according to A. E. Nordenskjöld, are rhombic bipyramids with the axial ratios $a:b:c=0{\cdot}692:1:0{\cdot}628$. The fused trioxide furnishes a hard, brittle, coral-red, crystalline mass, which forms a scarlet-red powder. L. Playfair and J. P. Joule gave 2·676 for the **specific gravity** of the crystallized trioxide; C. H. D. Bödeker gave 2·737 at 14°, and for that which had been fused, 2·629 at 14°, while A. Schafarik gave 2·819 at 20°; W. A. Roth and G. Becker, 2·80 at 21°; and E. Zettnow, 2·775 to 2·804. H. C. Jones and H. P. Bassett measured the sp. gr. of soln. with from 0·10 to 4·00 mols of $CrO_3$ per litre with the idea of calculating the solvation of chromium trioxide in soln.—*vide supra*. The sp. gr. of aq. soln. of the trioxide were determined by D. J. Mendeléeff, and E. Zettnow; the following are averages of the two sets of observations, at 15°:

| $CrO_3$ . | 5 | 10 | 15 | 20 | 30 | 40 | 50 | 60 per cent. |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. . | 1·0365 | 1·0760 | 1·1185 | 1·1640 | 1·2630 | 1·3780 | 1·5110 | 1·656 |

H. R. Moore and W. Blum found the sp. gr. at 25° of soln. of chromic acid containing at 25°, $C$ mols of $CrO_3$ per litre:

| $C$ . . | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. . | 1·0125 | 1·1383 | 1·2041 | 1·2699 | 1·3358 | 1·4016 | 1·4674 | 1·5332 | 1·5990 | 1·6648 |

W. Biltz discussed the mol. vol.; and C. del Fresno, the contraction in vol. which occurs when the compound is formed. The **viscosity,** $\eta$ (water unity) dynes per cm. for aq. soln. of chromium trioxide containing $\omega$ grm. $CrO_3$ per 100 grms. of water, is:

| | | | | | |
|---|---|---|---|---|---|
| 0° | $\omega$ . . | 111·4 | 72·86 | 51·38 | 29·59 |
| | $\eta$ . . | 1·482 | 1·195 | 1·110 | 1·057 |
| 18° | $\omega$ . . | 98·8 | 71·01 | 35·92 | 16·71 |
| | $\eta$ . . | 1·5116 | 1·2849 | 1·1017 | 1·0349 |
| 25° | $\omega$ . . | 147·4 | 89·40 | 42·68 | 12·05 |
| | $\eta$ . . | 2·3360 | 1·4880 | 1·1360 | 1·024 |
| 40° | $\omega$ . . | 111·4 | 72·86 | 51·38 | 16·55 |
| | $\eta$ . . | 1·328 | 1·164 | 1·1055 | 1·027 |

S. A. Mumford and L. F. Gilbert found the sp. gr. of soln. of chromic acid containing $M$ mols per litre at 25°/4°, to be:

| $M$ . . | 10·713 | 7·288 | 5·176 | 2·322 | 0·842 | 0·206 | 0·060 | 0·013 |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. . . | 1·7042 | 1·4835 | 1·3479 | 1·1530 | 1·0602 | 1·0119 | 1·0012 | 0·9981 |

and at 45°/4°:

| $M$ . . | 10·768 | 7·034 | 5·890 | 2·829 | 2·069 | 1·082 | 0·459 | 0·226 |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. . . | 1·6954 | 1·4593 | 1·3813 | 1·1831 | 1·1306 | 1·0599 | 1·0226 | 1·0063 |

G. G. and I. N. Longinescu calculated the sp. gr. of the soln. considered as a binary mixture. C. del Fresno, and D. Balareff studied the mol. vol. R. Dubrisay measured the **surface tension** during the progressive neutralization of chromic acid soln. by soln. of sodium hydroxide, and by ammonia, and found that chromic acid differs from a strong dibasic acid, such as sulphuric acid, in exhibiting a constant surface tension only until the first acid function is neutralized, after which the surface tension decreases gradually but slightly until the second is neutralized,

when, as usual, a great decrease occurs. T. Graham made observations on the rate of **diffusion** of chromium trioxide in aq. soln.

The **specific heat** of aq. soln. of chromium trioxide, between 21° and 53°, was measured by J. C. G. de Marignac.[4] E. H. Buchner and A. Prins gave for soln. with the molar ratio $CrO_3 : nH_2O$ :

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $n$ . . | 3·55 | 5·02 | 9·91 | 25·2 | 50 | 87·9 | 100·5 | 200 |
| Sp. ht. . | 0·506 | 0·557 | 0·665 | 0·803 | 0·876 | 0·927 | 0·942 | 0·970 |

The last two sets of data are by J. C. G. de Marignac. The subject was discussed by N. de Kolossowsky. O. Unverdorben, J. J. Berzelius, H. Moissan, E. Hintz, and A. Schafarik observed that when chromium trioxide is heated, it becomes almost black and then melts to a reddish-brown liquid. M. Traube gave 180°–190° for the **melting point**; F. M. Jäger and H. C. Germs, 198°; and E. Groschuff said that the trioxide melts at 196° with a little decomposition, and that the molten mass can be easily under-cooled 26°; E. Zettnow gave 170°–172° for the f.p., and said that on solidification, the temp. may rise to 193°; and that there is a large contraction on solidification. The **freezing points** of aq. soln. of chromium trioxide are indicated in Fig. 24. J. Koppel and R. Blumenthal gave:

| | | | | | |
|---|---|---|---|---|---|
| $CrO_3$ . . . | 23·1 | 28·6 | 44·4 | 50·0 | 54·5 per cent. |
| Freezing point . | −6° | −9·3° | −24° | −36° | −51° |

and W. Ostwald, and R. Abegg and A. J. Cox made observations on the mol. lowering of the f.p. of aq. soln. H. C. Jones and H. P. Bassett found that with soln. containing $m$ mol of $CrO_3$ per litre, the lowering of the f.p. was:

| | | | | |
|---|---|---|---|---|
| $m$ . . . . | 0·10 | 1·0 | 2·5 | 4·00 |
| Fall of f.p. . . . | 5·26° | 6·78° | 9·00° | 14·40° |

E. Cornec measured the lowering of the f.p. of aq. soln. of chromic acid during its progressive neutralization with sodium hydroxide. There is a break in the curve corresponding with the formation of the dichromate, and another break corresponding with the chromate. J. J. Berzelius, A. Schafarik, H. Moissan, and E. Hintz noticed that when heated to near the b.p. of sulphuric acid, chromium trioxide **volatilizes** forming reddish fumes. O. Unverdorben, A. Schafarik, and J. J. Berzelius observed that chromium trioxide decomposes above its m.p. into oxygen and chromic oxide with a glow, but if the chromium trioxide has been obtained by evaporation no glowing occurs. H. Arctowsky said that decomposition occurs at 200°; and I. Schukoff added that the trioxide decomposes with deflagration at 300°, with the evolution of oxygen. L. and P. Wöhler said that below 1200°, the reaction $2CrO_3 = Cr_2O_3 + 3O$ is not reversible and is probably exothermal; but in the presence of potassium sulphate, at 1000°, the reaction, $2K_2SO_4 + Cr_2O_3 + 3O \rightleftharpoons 2(K_2SO_4.CrO_3)$, is reversible, and at 1009°, the press. of the oxygen is 878 mm.; at 1029°, 785 mm. A. Simon and T. Schmidt's heating curve, and dissociation press. curve are shown in Fig. 22. K. S. Nargund and H. E. Watson found that 2 hrs.' heating at 300° resulted in a 28 per cent. decomposition; at 350°, 48 per cent.; at 400°, 52 per cent.; at 550°, 100 per cent.; 9 hrs. at 350°, 52 per cent., and 18 hrs. at 350°, 55 per cent. R. Read observed that in the non-luminous flame chromium trioxide decomposes with a bright, white incandescence. H. Arctowsky noticed that when heated to 125°, under 16 mm. press., chromium trioxide volatilizes forming a sublimate of long, red needles. J. Koppel and R. Blumenthal observed the **boiling points** of aq. soln. of chromium trioxide, at ordinary press.:

| | | | | | |
|---|---|---|---|---|---|
| $CrO_3$ . . | 10·81 | 24·08 | 45·15 | 61·54 | 71·24 per cent. |
| Boiling point | 102° | 102° | 110·5° | 120° | 127° |

and T. Costa found the mol. rise of the b.p. of aq. soln. to be:

| | | | | |
|---|---|---|---|---|
| $CrO_3$ . . | 1·5233 | 1·7886 | 3·8212 | 11·5159 per cent. |
| Rise of temp. . | 15·6° | 14·3° | 14·1° | 13·7° |

Observations were also made by E. Field—*vide supra*. W. G. Mixter gave for the **heat of formation** of chromium trioxide, $CrO_3$, from its elements, 140 Cals.; amorphous chromic oxide, 36·2 Cals.; and from crystalline chromic oxide 26·1 Cals., whilst M. Berthelot gave 26·2 Cals. W. A. Roth and G. Becker gave $(Cr,\frac{3}{2}O_2)=147{\cdot}1$ Cals.; and for the heat of reduction of $CrO_3$ to $Cr_2O_3$, −6·1 Cals. J. Thomsen gave for the heat of formation in aq. soln., 18·913 Cals., and M. Berthelot, 10·6 Cals. The subject was discussed by A. Berkenheim. According to F. Morges, the heat of solution of $CrO_3$ in water is $CrO_3+H_2O=H_2CrO_4+580$ cals.; for $H_2CrO_4+H_2O$, 340 cals.; for $H_2CrO_4.H_2O+H_2O=260$ cals.; for $H_2CrO_4.2H_2O+H_2O$, 135 cals.; $H_2CrO_4.3H_2O+H_2O$, 171 cals.; $H_2CrO_4.4H_2O+H_2O$, 80 cals.; $H_2CrO_4.5H_2O+H_2O$, 35 cals.; $H_2CrO_4.5H_2O+25H_2O$, 500 cals.; and $H_2CrO_4.30H_2O+25H_2O$, 210 cals. P. Sabatier gave 1·9 cals. for the heat of soln. in 40 times its weight of water at 19°. E. H. Büchner and A. Prins gave for the **heat of dilution** from $CrO_3.nH_2O$ to $CrO_3.80H_2O$, and the total heat of soln. when the heat of soln. for a mol of solid $CrO_3$ and 80 mols of water is 24·67 cals.:

| | | | | | | |
|---|---|---|---|---|---|---|
| $n$ . . . | 3·32 | 4·03 | 4·96 | 10·1 | 25·2 | 49·9 |
| Heat dilution . | 1447 | 1111 | 866 | 469 | 122 | 16 |
| Heat solution . | 1020 | 1356 | 1601 | 1998 | 2345 | 2451 |

J. Thomsen gave for the **heat of neutralization,** $(CrO_3,NaOH_{aq.})=13{\cdot}134$ Cals.; for $(CrO_3,2NaOH_{aq.})=24{\cdot}720$ Cals.; P. Sabatier gave $(2CrO_3,K_2O_{aq.})=27{\cdot}0$ Cals.; $(2CrO_3,2K_2O_{aq.})=50{\cdot}8$ Cals.; while M. Berthelot gave $(2CrO_3,K_2O_{aq.})=26{\cdot}8$ Cals.; $(2CrO_3,2NH_{3aq.})=24{\cdot}0$ Cals.; for solid chromium trioxide, $(CrO_3,K_2O)=95{\cdot}6$ Cals.; $(2CrO_3.K_2O)=106{\cdot}8$ Cals., when for solids $(SO_3,K_2O)=141{\cdot}4$ Cals., and $(2SO_3,K_2O)=167{\cdot}6$ Cals.

E. Cornec measured the **index of refraction** of a soln. of chromic acid during its progressive neutralization with potassium hydroxide and with aq. ammonia. The results show that the aq. soln. of the acid first furnishes dichromate, and as the proportion of base increases, chromate is formed. W. J. Pope [5] gave 37·13 for the refraction equivalent of the $CrO_4$-radicle. J. Piccard and E. Thomas discussed the colour of chromate and dichromate ions. The **absorption spectrum** of aq. soln. of chromium trioxide was examined by J. H. Gladstone.[6] J. M. Hiebendaal showed that the green and blue rays are absorbed by the soln. According to A. Étard, there is a fine absorption band between $\lambda=6870$ and 6800 with conc. soln.; but soln. of potassium chromate and dichromate do not show this band. H. Settegast measured the absorption spectrum; and P. Sabatier found that the coeff. of absorption, $\alpha$, for light of different wave-lengths, $\lambda$, is not sensibly affected by the thickness, $\lambda$, of the layer of liquid through which the light is passed. Here, $l=l_0 10^{-\alpha\lambda}$ with light of intensity $l_0$:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\lambda$ . . | 5450 | 5480 | 5550 | 5620 | 5690 | 5770 | 5850 | 5930 |
| $\alpha$ . . | 0·005 | 0·025 | 0·143 | 0·351 | 0·628 | 0·812 | 0·900 | 0·950 |

Beyond wave-length 5450 the coeff. becomes practically zero; in very dil. soln., the coeff. for wave-length 5180 is about 0·000013. The values are the same for the acid as for the salts, for solid potassium dichromate as for its soln., for the ammonium salt as for the potassium salt, and it follows that the absorption exerted by solid or dissolved alkaline dichromates is sensibly identical with that of the chromic acid which they contain. With soln. of potassium chromate, the absorption is in the blue and the violet, and with dilution, the absorption extends more in the direction of the red. Thus, O. Knoblauch found that in conc. soln., the absorption begins at 4900, and in dil. soln., at 5100. W. Böhlendorff obtained similar results; while J. M. Hiebendaal observed that the absorption begins at 5050, and in dil. soln. at 4770. K. Vierordt, P. Pogany, F. Grünbaum, A. Hantzsch, P. Bovis, N. R. Tawde and G. R. Paranjpe, G. Jander and T. Aden, M. N. Saha, C. P. Snow and F. I. G. Rawlins, and H. Settegast made observations on this subject: and P. Sabatier found that with potassium chromate soln., the coeff. of transmission, $a$,

for soln. with one eq. of salt per litre, and, $\alpha_2$, for soln. with 2 eq. per litre, were:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\lambda$ . | 4940 | 4990 | 5030 | 5060 | 5080 | 5110 | 5130 | 5180 | 5240 |
| $\alpha_1$ . | — | 0·06 | 0·18 | 0·325 | 0·44 | 0·61 | 0·69 | 0·85 | 0·92 |
| $\alpha_2$ . | 0·025 | 0·108 | 0·207 | 0·43 | 0·51 | 0·62 | 0·69 | 0·84 | 0·93 |

The absorption is slightly greater in the more dil. soln., and this points to slight dissociation with formation of some dichromate, which, however, is only produced in very minute quantity. H. Becquerel found that soln. of potassim chromate are transparent for the ultra-red rays; and G. Massol and A. Faucon studied the transmission of ultra-violet rays. D. Brewster investigated the absorption spectrum of soln. of ammonium chromate; and J. H. Gladstone, soln. of metal chromates. H. von Halban and H. Siedentopf found that a soln. of potassium chromate in 0·05*N*-KOH had the extinction coeff., $\epsilon$, for light of wave-length, $\lambda$, when $I=I_0 10^{-\epsilon Cd}$, where $C$ denotes the conc. in mols per litre.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\lambda$ . | 2540 | 2650 | 2970 | 3130 | 3340 | 2800 | 2890 | 3600 | 4360 |
| $\epsilon \times 10^{-3}$ | 2·35 | 3·00 | 0·927 | 0·1935 | 0·9850 | 3·290 | 2·086 | 4·416 | 0·3138 |

H. C. Jones and W. W. Strong found that the absorption spectra of conc. soln. of potassium chromate shows a stronger absorption than the value calculated from Beer's law. G. Rudorf discussed the applicability of Beer's law. F. Weigert, and H. von Halban and H. Siedentopf studied the absorption of light by mixed soln. of potassium chromate and copper sulphate. Observations on the absorption spectrum of soln. of potassium dichromate were made by H. Bremer, P. Glan, F. Grünbaum, H. C. Jones and W. W. Strong, B. K. Mukerji and co-workers, F. Melde, J. Müller, P. Pogány, P. Sabatier, H. Settegast, C. P. Smyth, G. Jander and T. Aden, and K. Vierordt. According to J. Formanek, aq. soln. of potassium dichromate absorb the blue and violet rays, and with decreasing concentration, the absorption extends in the direction of the red rays. O. Knoblauch found that with conc. soln., the absorption begins at 5200, and is complete at 4940, while with dil. soln., absorption begins at 5070, and is complete at 4840. W. Böhlendorff gave for the limit 5000, and J. M. Hiebendaal, 5250. A. Hantzsch's observations are summarized in Fig. 25. G. Hantzsch and R. H. Clark found that soln. of chromium trioxide in water and in aq. sulphuric acid are at all conc. optically identical with each other and with feebly acidic soln. of potassium dichromate. Soln. of the latter in water deviate very slightly in the direction of monochromate soln. Soln. of monochromates in water, in alkalis, and in methyl alcohol, are at all conc. quite different from dichromate and chromic acid soln. in their optical characteristics, but are identical among themselves, except for a slight deviation of the aq. soln. in the direction of the dichromate soln. The optical characteristics are independent, not only of the conc. and the solvent, but also of the temp. The chromophoric group in all acidic soln. is the completely saturated complex $Cr_2O_7$; in all alkaline soln. the corresponding complex is $CrO_4$. From the optical point of view, it is immaterial whether these complexes are combined with hydrogen or alkali metal, ionized or non-ionized; the colour of the ions must be the same as that of the non-ionized molecule. A. Hantzsch and C. S. Garrett explain the slight divergence from Beer's law with very conc., alkaline soln. of chromates by incomplete hydration rather than by ionization changes. All variations from the colorimetric law are attributed either to experimental errors, or to chemical changes between solvent and solute. H. M. Vernon estimated the degree of ionization from the colour

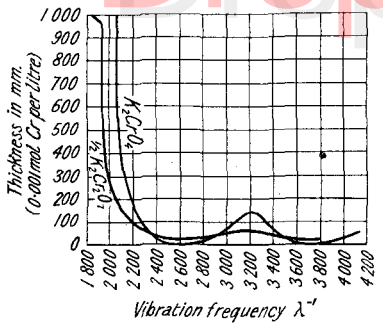



FIG. 25.—Absorption Spectra of Chromate Solutions.

of aq. soln. of the trioxide. E. Viterbi and G. Krausz measured the absorption spectra of soln. of chromic acid, and of potassium chromate and dichromate. There are seven feeble lines in the ultra-violet spectra of chromic acid and potassium dichromate which do not occur with soln. of the chromate. The bands with the chromate soln. are sharper than those with chromic acid or the dichromate. Except for a few minor differences, the spectra of the dichromate and of chromic acid are similar, and conform to Beer's law. Hence it is assumed that in these soln., the chromium is nearly all present as $Cr_2O_7''$, which has the same absorption spectrum either as an ion or as a non-ionized molecule; but probably with dil. soln. of the dichromate, there is some dissociation either as $Cr_2O_7''+H_2O \rightleftharpoons 2CrO_4''+2H^{\cdot}$, or as $Cr_2O_7''+H_2O \rightleftharpoons 2HCrO_4'$. Soln. of potassium chromate do not follow Beer's law, but the results with dil. soln. approach those with soln. of the dichromate, owing, probably, to a reaction $2CrO_4''+H_2O \rightleftharpoons Cr_2O_7''+2OH'$; and the addition of a large proportion of alkali displaces the equilibrium towards the left and restores the results for the absorption spectrum of the chromate. R. Robl observed but a faint luminescence in ultra-violet light; and A. Karl found the crystals triboluminescent. W. Spring found that there is a slight change of colour when soln. of potassium dichromate are allowed to stand. This shows that there is a change in the constitution of the soln. A. M. Taylor examined the **ultra-red spectrum**; D. M. Yost, the K-absorption spectrum; and N. Nisi, the **Raman effect**.

Both H. Buff,[7] and L. Bleekrode said that molten chromium trioxide is a good conductor of electricity, but J. W. Hittorf showed that the trioxide is a conductor only when it is contaminated with impurities, particularly water; the purified trioxide is a non-conductor. The **electrical conductivity** of aq. soln. was measured by R. Lenz, W. Ostwald, R. Abegg and A. J. Cox, E. Spitalsky, H. C. Jones and H. P. Bassett, etc. P. Walden found that with soln. containing a mol of the salt in $v$ litres of water at 25°, the mol. conductivities, $\mu$, are:

| $v$ | 16 | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|---|
| $\mu$ | 347·1 | 354·7 | 358·9 | 361·3 | 360·8 | 358·4 | 353·7 |

H. C. Jones gave for the molar conductivity, $\mu$, at 0°, and the percentage **degree of ionization**, $\alpha$,

| $v$ | 0·286 | 0·500 | 1·000 | 2·500 | 5·00 | 10·00 | 20·00 | 40·00 |
|---|---|---|---|---|---|---|---|---|
| $\mu$ | 108·4 | 206·8 | 312·4 | 388·9 | 420·0 | 436·0 | 440·0 | 452·0 |
| $\alpha$ | 20·7 | 39·3 | 59·7 | 74·3 | 80·3 | 83·4 | 84·1 | 86·4 |

The conductivity at infinite dilution is 523. The assumption that the ionization is represented by $H_2CrO_4=H^{\cdot}+HCrO_4'=2H^{\cdot}+CrO_4''$, does not explain the facts. The nature of the molecules formed in aq. soln. depends on the composition, concentration, and temp. of the soln. This has been the subject of many investigations and the results are usually expressed in the language of the ionic hypothesis. Whatever be the equilibrium condition, that state is quickly attained; and the result was shown by K. Beck and P. Stegmüller, T. Costa, M. S. Sherrill, and P. Walden to be independent of the mode of preparation of the soln. A. Hantzsch's optical measurements show that it is very improbable that chromium trioxide exists in aq. soln. as $CrO_3$, or in the ionic form $CrO_4''$ or $HCrO_4'$. He therefore assumed that in solid, and in aq. soln., the equilibrium condition: $nCrO_3+H_2O \rightleftharpoons (CrO_3)n.H_2O$, is almost wholly in favour of the polymerized product.

With the most concentrated soln. of chromium trioxide in water, it is probable that trichromic and tetrachromic acids are formed, but in more dilute soln., only monochromic and dichromic acids are involved; the former may be ionized: $H_2CrO_4 \rightleftharpoons H^{\cdot}+HCrO_4'=2H^{\cdot}+CrO_4''$, and the latter: $H_2Cr_2O_7 \rightleftharpoons H^{\cdot}+HCr_2O_7' \rightleftharpoons 2H^{\cdot}+Cr_2O_7''$. It was, therefore, inferred that chromic acid, $H_2CrO_4$, exists in soln., and that it behaves as a monobasic acid $H(HCrO_4)$, ionizing: $H_2CrO_4=H^{\cdot}+HCrO_4'$. R. Abegg and A. J. Cox took a similar view, and added that even with soln. of the dichromates, there is a relatively small proportion of $Cr_2O_7''$-ions, and that as the temp. rises, the $Cr_2O_7''$-ions form $CrO_4''$-ions and chromic acid.

E. Carrière and P. Castel studied the ionic equilibrium $2CrO_4'' + 2H^{\cdot} \rightleftharpoons Cr_2O_7'' + H_2O$ at 20° by the conversion of barium chromate into barium dichromate by the addition of a measured amount of hydrochloric acid, the end-point being reached when the soln. becomes clear. The hydrogen-ion conc. of the equilibrium mixture was calculated from the law of mass action applied to the ions concerned assuming complete ionization, and good agreement was found between the observed and calculated values for low conc. The conc. of acid required decreases with temp., and the equilibrium constant at 18° is $3 \times 10^{-15}$. P. Walden concluded from the small change in the electrical conductivity of the soln. between the dilutions $v=32$ and $v=1024$, that a strong monobasic acid is involved and that this is almost completely ionized with the dilution $v=32$. W. Ostwald, however, concluded that the acid exists in aq. soln., not as $H_2CrO_4$, but as $H_2Cr_2O_7$; and in support of this he showed that an aq. soln. which contains a mol of a compound per kilogram lowers the f.p. −1·85°. Acetic acid gives nearly the normal value −1·92°; nitric acid gives −3·70°, nearly twice the normal value, in agreement with the assumption that it is almost completely ionized into $H^{\cdot}$ and $NO_3'$ ions; sulphuric acid gives −2·00° in agreement with the assumption that it is ionized $H_2SO_4 \rightleftharpoons 2H^{\cdot} + SO_4''$ to the extent of about 0·6; and chromic acid gives −1·34° in agreement with the assumption that it is completely ionized $H_2Cr_2O_7 \rightleftharpoons 2H^{\cdot} + Cr_2O_7''$, and this is in accord with the observations of P. Walden. According to W. C. D. Whetham, the eq. conductivity, $\lambda$, of soln. of potassium dichromate containing $m$ eq. per litre is:

| $m$ | 0·00001 | 0·0001 | 0·001 | 0·01 | 0·1 | 0·2 |
|---|---|---|---|---|---|---|
| $\lambda$ | 81·3 | 76·3 | 71·4 | 70·4 | 64·3 | 61·5 |

The rise of the conductivity with dilution up to $m=0·0001$ is unusually small, and this is attributed to the hydrolysis of the $Cr_2O_7''$-ions to the slow-moving $HCrO_4'$-ions. The unusually large rise in the conductivity when the soln. is diluted from $m=0·0001$ to $m=0·00001$, is attributed to the ionization $HCrO_4' \rightleftharpoons H^{\cdot} + CrO_4''$ or possibly $HCr_2O_7' \rightleftharpoons H^{\cdot} + Cr_2O_7''$. H. R. Moore and W. Blum found the electrical conductivity $\kappa$ mhos of soln. of $C$ mols of chromic acid per litre at 25° to be:

| $C$ | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\kappa$ | 0° | 0·219 | 0·342 | 0·418 | 0·440 | 0·435 | 0·420 | 0·387 | 0·345 | 0·289 | 0·225 |
| | 25° | 0·315 | 0·513 | 0·616 | 0·657 | 0·662 | 0·641 | 0·600 | 0·545 | 0·477 | 0·402 |
| | 45° | 0·389 | 0·632 | 0·763 | 0·818 | 0·831 | 0·817 | 0·769 | 0·708 | 0·625 | 0·528 |

The resulting curves show a maximum for about $4M$-soln. at 0°; for $4·8M$-soln. at 25°; and for $5·0M$-soln. at 45°. This shift is greater than can be explained by the change in sp. gr. or in vol. conc. caused by the difference in temp.; it must therefore involve a difference in the degree or type of dissociation of the chromic acid. R. N. J. Saal found the equilibrium constant of the reaction $Cr_2O_7'' + H_2O \rightleftharpoons 2HCrO_4'$ to be 0·019. The decomposition of dichromate to chromate may occur (i) in the alkaline region: $Cr_2O_7'' + OH' \rightarrow CrO_4'' + HCrO_4'$; (ii) in the acidic and neutral region: $Cr_2O_7'' + H_2O \rightarrow 2HCrO_4'$; and (iii) diluting the soln. with acid and water: $Cr_2O_7'' + H^{\cdot} + H_2O (\rightleftharpoons HCr_2O_7' + H_2O) \rightarrow 2HCrO_4' + H^{\cdot}$. N. R. Dhar studied this subject. According to E. Spitalsky, the **hydrogen-ion concentration,** $[H^{\cdot}]$, in dil. soln. of chromic acid of [Cr], is:

| [Cr] | 0·002446 | 0·001218 | 0·000609 | 0·000602 | 0·000344 | 0·000172 |
|---|---|---|---|---|---|---|
| $[H^{\cdot}]$ | 0·00249 | 0·00121 | 0·000606 | 0·000595 | 0·000342 | 0·000166 |

so that the ratio $[H^{\cdot}]$ : [Cr] is nearly unity in harmony with the assumption that with dil. soln. of chromic acid, the ionization is: $H_2CrO_4 \rightleftharpoons H^{\cdot} + HCrO_4'$. The electrometric titration of chromic acid soln. was made by A. Miolati and E. Mascetti, N. H. Furman, R. N. J. Saal, Y. Kato and T. Murakami, W. S. Hughes, N. Westberg, and L. Margaillan. H. T. S. Britton obtained the results summarized in Fig. 26, by means of the hydrogen electrode; analogous results were obtained with the oxygen electrode. It follows that chromic acid ionizes as a normal dibasic acid. The

reaction $H_2CrO_4 \rightleftharpoons H^{\cdot} + HCrO_4'$ is almost complete in dil. soln., whereas the reaction $HCrO_4' \rightleftharpoons H^{\cdot} + CrO_4''$ is extremely small. A. Miolati and E. Mascetti measured the conductivity of soln. of chromic acid during its progressive neutralization with sodium hydroxide; E. Cornec made analogous observations with respect to the f.p., and indices of refraction of soln. of chromic acid being neutralized with sodium, potassium, or ammonium hydroxide; by L. Margaillan, on the e.m.f. of hydrogenized platinum and the soln. against a mercury cathode; and by R. Dubrisay, on the surface tension of the soln. In general, the soln. first forms the dichromate, and as more base is added, the chromate appears. This agrees with the assumption that the aq. soln. contains dichromic acid; and the result was confirmed by the observations of A. K. Datta and N. R. Dhar with respect to the index of refraction, and mol. vol. in soln.; by T. Costa, with respect to the b.p. of the soln.; and by H. C. Jones and H. P. Bassett, with respect to the f.p. of the soln.

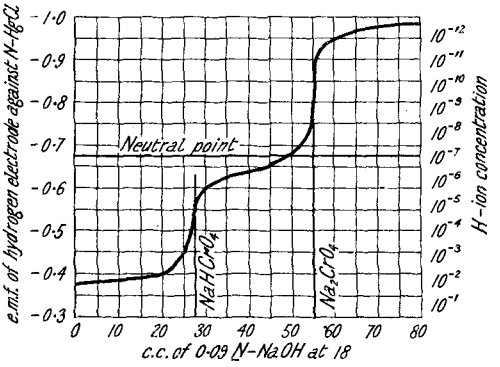



FIG. 26.—Electrometric Titration of Chromic Acid Solutions.

M. S. Sherrill attempted to reconcile the opposing hypothesis as to the nature of the ions in aq. soln. The depression of the f.p. of dil. soln. of chromic acid and potassium dichromate corresponds with their complete ionization into $Cr_2O_7''$-, and $H^{\cdot}$- or $K^{\cdot}$-ions, but the presence of some $HCrO_4'$-ions was assumed. The **ionization constant** for $2HCrO_4' \rightleftharpoons Cr_2O_7'' + 2H^{\cdot}$, was $K_1 = [Cr_2O_7'']/[HCrO_4']^2$, where $K_1 = 27$ with chromic acid soln., and 61 with soln. of potassium dichromate. From observations with ammonium chromate in dil. soln. in the presence of enough ammonia to prevent hydrolysis, $K_2 = [H^{\cdot}][CrO_4'']/[HCrO_4']$, where $K_2 = 5{\cdot}7 \times 10^{-7}$ at 18°; and from the partition of ammonia between aq. soln. of ammonium chromate, and chloroform, $K_2 = 6{\cdot}2 \times 10^{-7}$ at 18°, and $7{\cdot}4 \times 10^{-7}$ at 25°, so that the strength of chromic acid is about $\frac{1}{30}$th of that of acetic acid. H. T. S. Britton gave $4{\cdot}4 \times 10^{-7}$ for the second ionization constant at 18°; N. R. Dhar gave $K_2 = 5 \times 10^{-8}$; and W. S. Hughes, $K_2 = 10^{-7}$. W. V. Bhagwat and N. R. Dhar studied the subject. For H. Moissan's, and E. H. Riesenfeld and H. E. Wohler's observations on the electrolysis of soln. of chromic acid, *vide infra*, perchromic acid.

Attempts have been made to find the strength of chromic acid relatively with those of other acids. H. Settegast showed spectroscopically that chromic acid is displaced from chromates by sulphuric, formic, acetic, butyric, and tartaric acids. P. Sabatier showed colorimetrically that sulphuric, hydrochloric, phosphoric $H(H_2PO_4)$, and trichloracetic acids completely displace chromic acid from chromates. With acetic acid and the three equal acidic hydrogen atoms of citric acid, the action does not proceed quite so far. It is still less with the first acidic hydrogen of carbonic acid and the second acidic hydrogen of phosphoric acid, whilst the second acidic hydrogen of carbonic acid, boric acid, and the third acidic hydrogen of phosphoric acid have very little action at all. If the normal chromate is treated with an excess of solid boric acid, there is considerable formation of dichromate, owing to the production of an insoluble acid borate, the precipitation of which tends to make the action complete. From thermal data: $(K_2CrO_4, HCl) = 2{\cdot}4$ Cals.; and $(K_2Cr_2O_7, 2HCl) = -0{\cdot}2$ Cal., M. Berthelot showed that hydrochloric acid should convert chromates into dichromates. He also found $(K_2CrO_4, 6H_2SO_4) = 0{\cdot}76$ Cal.; $(K_2CrO_4, CH_3COOH) = 1{\cdot}5$ Cals.; and $(K_2CrO_4, CO_2) = -0{\cdot}4$ Cal.; and added that in soln. of neutral potassium chromate, strong acids cause the total,

and weak acids the partial displacement of one of the two potassium-atoms, potassium dichromate being formed at the same time. This displacement is due not so much to the smaller heat of formation of the chromates compared with other acids capable of displacing chromic acid, as to the fact that the heat of formation of the dichromate is much greater than that of the neutral chromate, and that hence there is always a great tendency to the formation of the dichromate. This tendency renders the one potassium-atom in the neutral chromate easily replaceable—*vide infra*, the action of acids on potassium chromate. W. V. Bhagwat and N. R. Dhar favoured the view that chromic acid exists in soln. as $H_2CrO_4$, and potassium dichromate as $KHCrO_4$.

E. Spitalsky measured the catalytic effect of soln. of chromic acid on the decomposition of ethyl diazoacetate by G. Bredig's process. Dil. soln. of chromic acid contain almost exclusively the dibasic acid $H_2Cr_2O_7$, which in a dilution of 500 litres is dissociated almost completely into $H^{\cdot}$- and $Cr_2O_7''$-ions. Dil. soln. of potassium dichromate contain almost exclusively the ions of the normal salt, $K_2Cr_2O_7$. In accordance with this view, dil. soln. of potassium chromate, $K_2CrO_4$, behave like alkalies to chromic acid, inasmuch as the $CrO_4''$-ions are changed almost quantitatively into $Cr_2O_7''$-ions, and the soln. remains neutral. Conc. soln. of potassium dichromate are slightly acid, probably owing to slight hydrolysis according to the equation : $Cr_2O_7'' + H_2O \rightleftharpoons 2CrO_4'' + 2H^{\cdot}$ ; the corresponding equilibrium constant $K_1=[CrO_4'']^2[H^{\cdot}]^2/[Cr_2O_7'']$ is $5{\cdot}1\times10^{-12}$. In a 0·1 molar soln. of the dichromate, the $Cr_2O_7''$-ions are hydrolyzed to the extent of 0·13 per cent. and in a 0·017 molar soln. to 0·28 per cent. so that the degree of hydrolysis does not alter much with dilution. Besides the hydrolysis, another reaction represented by the equation $CrO_4'' + H^{\cdot} \rightleftharpoons HCrO_4'$ takes place to some extent in dichromate soln. ; the corresponding constant $K_2=[CrO_4'']/[H^{\cdot}][HCrO_4']$ is $2{\cdot}7\times10^{-7}$. There is no evidence of the existence in dichromate soln. of complex ions such as $Cr_3O_{10}''$. J. Sand and K. Kästle showed that the acid resulting from the hydration of chromium trioxide is of medium strength, and suggested that in dichromate soln. there is the hydrolytic equilibrium : $Cr_2O_7'' + H_2O \rightleftharpoons 2CrO_4'' + 2H^{\cdot}$, and in that case, from observations on a mixture of potassium iodate and iodide, the reaction $3Cr_2O_7'' + 5I' + IO_3' = 6CrO_4'' + 3I_2$ is accelerated by $H^{\cdot}$-ions. The value of $K=[CrO_4'']^2[H^{\cdot}]^2/[Cr_2O_7'']$ calculated from these results is only approximately constant, and amounts to about $K=1{\cdot}5\times10^{-13}$ at 25° ; and hence it follows that 0·1*N*-$K_2Cr_2O_7$ is hydrolyzed to the extent of about 0·18 per cent. The deviation from constancy is not due to the direct action of dichromate on potassium iodide, as the rate of reaction between these substances is much slower than the main reaction. The disturbance is probably due to the catalytic effect of some product formed during the reaction.

J. Lundberg studied the effect of chromate soln. on the hydrolysis of ethyl acetate. If the hydrolysis of potassium chromate proceeds : $CrO_4'' + H_2O = HCrO_4' + OH'$, the equilibrium constant $K_1=[HCrO_4'][OH']/[CrO_4'']$ ; and if $2CrO_4'' + H_2O = CrO_7'' + 2OH'$, then $K_2=[Cr_2O_7'']^{\frac{1}{2}}[OH']/[CrO_4'']$ ; both values were too irregular to decide which is correct, but conductivity measurements favour the former, and for 0·1*N*-$K_2CrO_4$, $K_1=1{\cdot}368\times10^{-7}$, and 0·012 per cent. of the salt is hydrolyzed ; and in a 0·1*N*-$K_2Cr_2O_7$, containing chiefly $HCrO_4'$-ions, the salt is hydrolyzed to the extent of 0·094 per cent. in accord with $HCrO_4' = H^{\cdot} + CrO_4''$. Unlike E. Spitalsky, J. Lundberg assumes that a comparatively large proportion of $HCrO_4'$-ions is present in aq. soln. of potassium dichromate. For the observations of V. K. la Mer and C. L. Read, *vide infra*, sodium dichromate.

Observations on soln. of sparingly soluble chromates and dichromates have been made. Thus, R. Abegg and R. J. Cox studied the hydrolysis of mercuric chromate ; M. S. Sherrill, silver chromate ; and K. Beck and P. Stegmüller, lead chromate. From these results M. S. Sherrill calculated $[H^{\cdot}][CrO_4'']/[HCrO_4'] = 8{\cdot}4\times10^{-7}$ at 25° and $[HCrO_4']^2/[Cr_2O_7''] = 0{\cdot}013$ at 25° ; and K. Beck and P. Stegmüller, $[H^{\cdot}][CrO_4'']/[HCrO_4'] = 5{\cdot}7\times10^{-7}$ at 18°, and $[HCrO_4']^2/[Cr_2O_7'] = 2{\cdot}5$ at 18°.

Transport experiments on potassium chromate were made by J. F. Daniell and W. A. Miller, J. W. Hittorf, R. Lenz, O. Masson, B. D. Steele, R. B. Denison, and A. Charpentier; F. Kohlrausch calculated 72 for the **transport number** of $\frac{1}{2}CrO_4''$ from the conductivity data of calcium chromate; and M. S. Sherrill, 76·7 from the data of ammonium chromate; and 40 for the $HCrO_4'$-ion. W. Hittorf, E. H. Riesenfeld, and A. Charpentier made observations with potassium dichromate; and C. W. D. Whetham found the velocity of migration of the $Cr_2O_7$-ion to be 0·00047 cm. per sec. for a potential difference of one volt; and the transport number to be 91.

F. Morges found that the **electrolysis** of aq. soln. of chromium trioxide furnishes oxygen at the anode, and hydrogen and chromic chromate at the cathode. E. H. Riesenfeld found that in sulphuric acid soln. a perchromic acid is formed at the cathode. According to E. Liebreich, the thin layers of oxide or hydroxide on the cathode, which give rise to the periodic phenomena observed during the electrolysis of chromic acid are colloidal in nature; the oxide is drawn to the cathode just so long as a negative tension lies on it. The addition of chlorides brings about a displacement of two curves which make up the decomposition voltage curve of chromic acid. G. S. Forbes and P. A. Leighton studied the cathodic reduction of chromic acid to a chromic salt, and found the electrochemical yields with the cathode in light were about half per cent. greater than in darkness. Part or all this can be attributed to local heating in the thin diffusion layer above the cathode. The absence of any increase in the photochemical yield in light is compatible with light-sensitive chromate if the latter is equally reactive electrochemically before and after excitation. Granting that the slightly greater electrochemical efficiency in light is in part due to excited chromate, any estimate of the quantum yield requires several assumptions, especially one concerning the life of the excited individual upon which its chance of reaching the cathode depends. The subject was investigated by E. Müller and P. Ekwall, D. T. Ewing and co-workers, and A. Lottermoser and H. Walde. E. Liebreich showed that the thin layers of oxide or hydroxide, formed in the cathode during the electrolysis of soln. of chromic acid, are colloidal; they may give rise to colloidal phenomena; and the addition of chlorides displaces the two curves which make up the decomposition voltage of chromic acid. According to G. P. Vincent, the depolarizing action of a sat. soln. of potassium dichromate on hydrogen liberated at a smooth platinum electrode commences only when about 0·28 per cent. by vol. of conc. sulphuric acid is present. With a clean mercury cathode, the neutral soln. shows 100 per cent. depolarization of the hydrogen set free. The corrosion of zinc, iron, and copper by sat. soln. of potassium dichromate is produced only when the soln. is acidified. No corrosion occurs with sat. soln. of potassium dichromate when copper is short-circuited with mercury or platinum; or when iron is short-circuited with mercury. Zinc when short-circuited with mercury corrodes slightly, and more rapidly in 0·02 per cent. acetic acid soln. than in 0·02 per cent. sulphuric acid soln.

The data of L. Scherbakoff and O. Essin favour the view that in the electrolysis of conc. sulphuric acid soln. of chromic acid chromium is deposited by the discharge of chromic ions, but, according to E. Liebreich, with soln. in dil. acids, the data for current efficiencies favour the view that the metal is deposited by the discharge of chromous ions. S. Takegami studied the anodic oxidation of cathodically reduced chromic acid.

W. D. Bancroft measured the **oxidation potential** of potassium dichromate and chromic acid respectively at 16°–18°, and in 0·2*M*-soln. with the following results: stannous chloride and potash-lye, 1·37, and 1·70 volt; stannous chloride and hydrochloric acid, 0·57, and 0·90 volt; sodium sulphide, 1·15, and 1·49 volt; hydroxylamine and potash-lye, 1·12, and — volt; hydroxylamine and hydrochloric acid, 0·43, and — volt; chromous acetate, 0·70, and 1·03 volt; chromous acetate and alkali-lye, 1·09, and — volt; pyrogallol and potash-lye, 0·98, and 1·32 volt; hydroquinone and potash-lye, 0·83, and 1·17 volt; sodium hyposulphite, 0·78, and 1·12 volt; sodium

thiosulphate, 0·49, and 0·89 volt; sodium sulphite, 0·48, and 0·81 volt; sodium hydrosulphite, 0·40, and 0·73 volt; sulphurous acid, 0·35, and 0·68 volt; sodium hypophosphite, 0·55, and 0·88 volt; sodium phosphite, 0·47, and 0·80 volt; potassium arsenite, 0·56, and 0·89 volt; potassium ferrous oxalate, 0·78, and — volt. potassium ferrocyanide, 0·47, and 0·80 volt; potassium ferrocyanide and potash-lye, 0·59, and 0·93 volt; iodine and potash-lye, 0·57, and 0·91 volt; ferrous sulphate and sulphuric acid, 0·27, and 0·60 volt; ferrous sulphate, 0·43, and 0·76 volt; and cuprous chloride, 0·50, and 0·84 volt. B. Neumann measured the **potential** of the chromate electrode towards a normal electrode, and found for $N$-$K_2Cr_2O_7$, 0·79 volt; and for $N$-$H_2Cr_2O_7$, 1·11 volt. R. Ihle gave for sulphuric acid soln., —1·44 volt, and for alkaline soln., —0·46 volt; W. Hittorf, 1·2 volt; and F. Crotogino, 1·1 to 1·2 volt. The subject was investigated by K. F. Ochs. According to G. S. Forbes and E. P. Bartlett, certain reducing agents increase the oxidation potential of dichromate ions on platinum by amounts up to 0·2 volt—*e.g.* ferrous salts; and, according to L. Loimaranta, iodides. The phenomenon was discussed by R. Abegg, and R. Luther.

R. Luther emphasized the fact brought out by the observations of W. D. Bancroft, and B. Neumann, that the potential of chromic acid, and dichromates is augmented by increasing the acidity of the soln. Thus, if [H˙] denotes the conc. of the hydrogen ions, then, the oxidation potentials, $E$ volt, referred to the hydrogen electrode, are:

| [H˙] | . | 1 | 0·1 | 0·01 | 0·001 | 0·0001 | 0·00001 | 0·000001 |
|---|---|---|---|---|---|---|---|---|
| $E$ | . | 1·29 | 1·05 | 0·91 | 0·86 | 0·81 | 0·75 | 0·66 |

The chromic oxide-chromic acid potential given by R. Abegg and co-workers for $Cr^{\cdots}+4H_2O+3\oplus \rightleftharpoons HCrO_4'+7H^{\cdot}$ is nearly 1·3 volt. In alkaline soln., the potential referred to the normal electrode for $Cr(OH)_{3solid}+5OH'+3\oplus \rightleftharpoons CrO_4''+4H_2O$, is —0·1 volt, and E. Müller gave 0·908 for the e.m.f. of the cell Pt | $H_2$, 0·01$N$-KOH | 0·01$N$-KOH, 0·025$K_2CrO_4$ | Pt. E. Spitalsky found the potential of a dichromate soln. to be about 0·85 volt in the presence of an H˙-ion concentration of $10^{-3}$ to $10^{-4}$. R. Luther observed that the oxidation of chromium, and bi- and ter-valent chromium to chromate ions yield an e.m.f. corresponding with 0·6 volt for $Cr_{metal} \rightarrow CrO_4''$ against a normal electrode; 1·1 volt for $Cr^{\cdot\cdot} \rightarrow CrO_4''$; and 1·5 volt for $Cr^{\cdots} \rightarrow CrO_4''$. In acidic soln., the $CrO_4''$-ion plays only a secondary part. In the case of $HCrO_4'$-ions, the e.m.f. are 0·4 volt for $Cr_{metal}+4H_2O+6\oplus \rightarrow HCrO_4'+7H^{\cdot}$; 0·9 volt for $Cr^{\cdot\cdot}+4H_2O+4\oplus \rightarrow HCrO_4'+7H^{\cdot}$; and 1·3 volt for $Cr^{\cdots}+4H_2O+3\oplus \rightarrow HCrO_4'+7H^{\cdot}$. These changes furnish $Cr_{metal} \rightarrow Cr^{\cdot\cdot}$, 0·3 volt; $Cr_{metal} \rightarrow Cr^{\cdots}$, 0·2 volt; $Cr^{\cdot\cdot} \rightarrow Cr^{\cdots}$, 0·1 volt. If an intermediate oxidation compound exists under the conditions of observation, this compound is a stronger oxidizing agent than the highest oxidation product, and a stronger reducing agent than the lowest oxidation product.

H. Moissan [8] said that aq. soln. of chromium trioxide are **photosensitive,** for they decompose with the evolution of oxygen, when exposed to light. M. Ponton found that although chromates are stable in light, they are rapidly reduced if organic substances be present—*e.g.* ammonium or potassium dichromate in contact with paper. J. M. Eder observed that glue, albumin, gum arabic, dextrine, cane-sugar, grape-sugar, glycerol, caseïn, alcohol, etc., act in this way. E. Kopp said that chromic oxide is formed. The reaction was observed by W. H. F. Talbot, A. Poitevin, and J. C. Schnauss. E. Goldberg said that the reaction between quinine and chromates is activated by light; but R. Luther and G. S. Forbes showed that the photoactivation of the chromate is negligibly small in comparison with that of the quinine. The subject was discussed by J. Plotnikoff, H. C. Winther, E. J. Bowen and C. W. Bunn, H. Zocher and K. Coper, B. K. Mukerji and N. R. Dhar, F. Weigert, G. S. Forbes and co-workers, M. Schiel, F. Schömmer, G. S. Forbes and P. A. Leighton, and R. E. Liesegang. J. Plotnikoff found that the chromate of ammonium, potassium or sodium suffers no decomposition when exposed to the most intense sunlight provided substances capable of oxidation

are absent; if organic substances are present, reduction occurs even in the light from an electric arc; the reduction results in the formation of a brown precipitate or of a green soln. according to the nature of the oxygen acceptor; and gas may be evolved in some cases—*e.g.* ammonia from ammonium chromate. The photo-sensitiveness of mixtures of gelatine or glue and chromates is of industrial importance—the organic substance becomes insoluble and the chromium trioxide is reduced. J. M. Eder showed that in this respect, the dichromates are more sensitive than the chromates. A. Popovicky suggested that the substance obtained when gelatin treated with a dichromate is exposed to sunlight is the compound, $4Cr_2O_3.3CrO_3$; the tanning action on gelatin is attributed to this compound. J. M. Eder found that the action of light on chromated gelatin begins at 550$\mu\mu$, reaches a maximum between 470$\mu\mu$ and 430$\mu\mu$, and becomes very slight beyond 380$\mu\mu$. This is in contrast with J. Plotnikoff's result with collodion sensitized with potassium dichromate and cresyl-blue in which the action was found to begin in the yellow at 595$\mu\mu$, and reached a maximum in the green between 540$\mu\mu$ and 580$\mu\mu$. A photographic reproduction process is based on the reaction; and chromated and insolated glue can in some cases be used as a substitute for wood, leather, or celluloid. According to T. Swensson, the potential of soln. of potassium dichromate against a platinum electrode, and exposed to the ultra-violet light of a mercury lamp, rises rapidly, and on removing the light, it slowly falls. The same result is obtained whether or not the platinum electrode is illuminated. A soln. with 4 mols of sulphuric acid and a mol of potassium dichromate per litre, gives an increase of potential of 0·2280 volt by illumination. The cause of the large change in potential is in some way due to a mutual action of the dichromate and sulphuric acid, since both potassium dichromate soln. and sulphuric acid when submitted alone to the action of the light only give a lowering of the potential, whereas chromic acid soln. gives a slight increase. The increase of potential is independent of the conc. of the soln. E. Müller studied the potential-current curves of 30 per cent. soln. of chromium trioxide, from which it is inferred that a film of chromic oxide is formed at cathode potentials not exceeding 0·3 volt. This film hinders the excess of chromium ions, but is permeable to hydrogen ions. At about —0·7 volt, the film begins to be permeable and an almost continuous reduction of sexivalent to tervalent chromium sets in; and with still more negative values, the deposition of chromium begins, and the film disappears. In the presence of $SO_4$-, $NO_3$-, $ClO_4$-, and $SiF_6$-ions, the film is imperfect and may be swept away by the gaseous hydrogen which is evolved—hence the presence of sulphates favours the deposition of bright, coherent chromium. The periodic phenomenon in the electrolysis of chromic acid was discussed by J. E. Liebreich, G. J. Sargent, A. Kleffner, and K. Oyabu. A. V. Pamfiloff discussed the *rôle* of chromates in the electroytic production of chlorates; and D. J. MacNaughtan and R. A. F. Hammond, in the electrodeposition of nickel.

According to E. Wedekind and C. Horst,[9] the **magnetic susceptibility** of chromium trioxide is $0·75\times10^{-6}$ mass units; K. Honda and T. Sone gave $0·51\times10^{-6}$ at 18°, and at 225°, L. Blanc, and L. A. Welo made some observations on this subject. P. Pascal gave $-0·5\times10^{-5}$ for the mol. magnetic susceptibility of chromic acid.

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## § 14. The Chemical Properties of Chromium Trioxide

According to J. J. Berzelius,[1] and O. Unverdorben, chromium trioxide has no smell; it tastes first acidic, then harsh, but not metallic; and it stains the skin yellow—the stain is not removed by water but it is removed by alkalies. Chromium trioxide solid or in aq. soln., or in sulphuric acid soln., or in the form of its salts, is a strong oxidizing agent, and is therefore reduced by many agents. E. Ludwig observed that **hydrogen** quickly reduces a conc. soln. of chromium trioxide, but acts only slowly on a dil. soln. W. N. Ipatieff and co-workers found that an acidic neutral or alkaline soln. of chromium trioxide at 280° to 300° is reduced by hydrogen under a press. of 200 atm. to form crystals of $Cr_2O_3.H_2O$. In the presence of free sulphuric acid at 300° and 80 atm., small violet-grey crystals, soluble in neither acid nor alkali, are formed and, in the latter case, appear to have the composition $R_2O.2Cr_2O_3.3SO_3.H_2O$. At 280° and 150 to 200 atm., the compound $2Cr_2O_3.3SO_3.6H_2O$ is obtained as dark green, cubic crystals. In the presence of ferrous or ferric sulphate, complex isomorphous mixtures containing iron and chromium are obtained in the form of dark green, cubic crystals. Iron pyrites frequently accompanies such mixtures—*vide supra*, chromic oxyhydroxide. C. L. Reese observed that in the absence of a catalytic agent, a soln. of chromic acid, alone or in the presence of 1 to 15 per cent. by vol. of sulphuric acid, is not reduced by hydrogen below 50°; and only very slowly below 100°. After 116 hrs.' exposure, at 100°, 70 per cent. of hydrogen is oxidized; and at 156°, with 7 hrs.' exposure, 11 per cent. of hydrogen is oxidized and much oxygen is evolved owing to the decomposition of the chromic acid. The oxidation is not dependent on the thermal decomposition of chromic acid because it occurs at a temp. below that at which oxygen is evolved. An aq. soln. of chromic acid is not reduced by the hydrogen evolved by passing an electric current through the liquid, but if a trace of sulphuric acid or a sulphate be present, reduction occurs until a certain limit is reached, and this is dependent on the conc. of the acid. A. C. Chapman found that acidic soln. of chromates are reduced to chromic salts by hydrogenized palladium. J. Hargreaves and T. Robinson observed the reduction of chromates to chromic oxide when heated in hydrogen. Purified chromium trioxide exposed to **air** slowly becomes moist, and deliquescent. A. Mailfert found that in the presence of ether, **ozone** furnishes perchromic acid; but H. Moissan could not obtain blue perchromic acid by the action of ozone on a soln. of chromic acid. Chromium trioxide was found by H. Rose to dissolve in a small proportion of **water** forming a dark reddish-brown soln., and with a larger proportion of water, the colour is lemon-yellow. The aq. soln. reddens litmus. For the solubility in water, *vide supra*. According to M. Traube, in acidic soln., chromium trioxide is reduced by **hydrogen dioxide** to chromic oxide: $4CrO_3+8H_2O_2+6H_2SO_4=2Cr_2(SO_4)_3+7O_2+14H_2O$. L. C. A. Barreswil observed that a transient blue colour is produced before the evolution of oxygen begins—*vide infra*, perchromic acid. The reaction was discussed by A. Bach, E. Spitalsky, A. von Kess and F. E. Lederer, E. Spitalsky and N. Koboseff, and E. H. Riesenfeld and A. Wesch. The catalytic decomposition of potassium dichromate and hydrogen dioxide by cobalt salts is represented: $K_2Cr_2O_7+H_2O_2=2KCrO_4+H_2O$, and $2KCrO_4+H_2O_2=K_2Cr_2O_7+H_2O+O_2$. The velocity of the reaction is promoted by copper, manganese, nickel, and cerium salts. In that case, the reaction $2KCrO_4+H_2O_2=K_2Cr_2O_7+H_2O+O_2$ then gives way to the rapid reaction $2KCrO_4+CoCl_2+2H_2O=H_2CoO_3+K_2Cr_2O_7+2HCl$, and $H_2CoO_3+H_2O_2+2HCl=CoCl_2+3H_2O+O_2$, in agreement with the observation that a definite $H^{\cdot}$-ion conc. is necessary for the promotion. This explanation agrees with the observation that a definite hydrogen-ion conc. is necessary for the promotion. Oxidation of the cobalt is indicated by a decrease in the conc. of the perchromic acid in the promoted reaction. The cobalt may be in the ter- or quadri-valent state during the promotion. The catalytic decomposition of hydrogen dioxide by potassium dichromate was studied by E. Spitalsky and N. Koboseff; and its acceleration by manganese salts by

A. C. Robertson. According to E. Spitalsky and N. Koboseff, during the catalysis of hydrogen dioxide by chromic acid or by acidified soln. of potassium dichromate the conductivity at first decreases sharply to a value which remains approximately constant during the major part of the reaction and then returns to its initial value as the reaction approaches completion. These changes are due to the formation and decomposition of catalytic intermediate compounds, and are, as is the catalysis itself, completely reversible, so that for each initial conc. of the substrate a definite value is obtained for the conductivity decrease and for the minimum conductivity. That the conductivity changes afford a parallel with the complicated kinetics of the reaction in dil. acid soln. is indicated by the coincidence of the maxima of the velocity of catalysis and of the velocity of the conductivity change. From the decrease of the conductivity the extent to which the hydrogen ions are used up in the formation of intermediate compounds may be calculated; the flat portion of the velocity curves represents the complete removal of the hydrogen ions, whilst the velocity maximum expresses their liberation near the end of the reaction. The relationships have been determined at constant substrate conc. of the reaction velocity and of the conductivity decrease with (1) variation of the dichromate conc. at constant acid conc.; (2) variation of the acid conc. at constant dichromate conc.; and (3) variation in constant ratio of both the acid and dichromate conc. In the third case only the reaction velocity and the conductivity decrease are influenced in the same manner by the conc. changes. The nature of the curves obtained leads to the hypothesis that during the course of the reaction two intermediate compounds, $M_1$ and $M_2$, are formed reversibly, which require no hydrogen ions for their formation and possess relatively small affinity constants, together with a third compound $M_3$, which is much more stable and requires hydrogen ions for its formation. From the initial acid and dichromate concentrations and the decrease of hydrogen-ion conc. during the catalysis the most probable nature of the more stable compound $M_3$ is given by the equation: $2Cr_2O_7'' + 2H_2O_2 + K^{\cdot} + H^{\cdot} = KH_5Cr_4O_{18}''$, the affinity constant of the reaction being $10^{13}$. The velocity constants $k_1 = 42$, and $k_2 = 5{\cdot}6$. On the flat portion of the velocity curve, where, at high concentrations of hydrogen peroxide, the more stable additive compound $M_3$ is but little dissociated, the catalysis is effected simultaneously by two intermediate compounds, viz., $M_3$ and the compound $M_1$, which is the active agent in the catalysis in neutral soln. Towards the end of the reaction, as the hydrogen peroxide conc. becomes very small, $M_3$ decomposes and releases the hydrogen ions; very active but short-lived intermediate compounds are then formed, and account for the sharp maximum in the reaction velocity. From the affinity constants of $M_1$ and $M_3$, bearing in mind the possible existence of another substance $M_2$, the reaction velocity curves agree fairly well with part of the experimental curves.

According to H. Moissan,[2] chromium trioxide does not react with **chlorine** free from hydrogen chloride; and K. H. Butler and D. McIntosh observed that the trioxide is insoluble in liquid chlorine, and has no effect on the b.p. of the liquid. According to A. Michael and A. Murphy, a soln. of chlorine in carbon tetrachloride in a sealed tube at 175° forms chromyl and carbonyl chlorides. H. Moissan observed that **bromine** has no action on the trioxide. I. Walz found that a conc. soln. of chromium trioxide, when poured on **iodine,** rapidly turns black and assumes a syrupy consistency, and the liquid thus formed does not respond to the tests for free iodic or hydriodic acid; chromium hypoiodite may be formed. A mixture of sulphuric acid and chromium trioxide oxidizes iodine to iodic acid. O. Ruff and H. Krug found that the trioxide is vigorously attacked by **chlorine trifluoride.** L. Henry showed that **hydrogen chloride** forms chromyl chloride: $CrO_3 + 2HCl = CrO_2Cl_2 + H_2O$. The water so formed reacts with the chromyl chloride producing a dark oily liquid. W. Autenrieth added that the reaction with dry hydrogen chloride is vigorous and chromyl chloride is formed; with 35 to 40 per cent. **hydrochloric acid,** 35 per cent. of the acid forms chromyl chloride: $CrO_3 + 2HCl = CrO_2Cl_2 + H_2O$; with 20 per cent. hydrochloric acid, chlorine, as well as chromyl chloride, is produced:

$2CrO_3+12HCl=2CrCl_3+3Cl_2+6H_2O$. F. Penny said that with boiling hydrochloric acid chromic chloride and chlorine are formed. J. W. Thomas found that hydrogen chloride reduces chromates and dichromates. R. J. Meyer and H. Best obtained chromyl chloride by the action of hydrogen chloride on an acetic acid soln. of chromium trioxide. H. Moissan found that dry **hydrogen bromide** does not act on chromium trioxide; while, according to F. Penny, boiling **hydrobromic acid** yields bromine. M. Bobtelsky and A. Rosenberg found that the velocity measurements agreed with the typical formula for a reaction of the second order; and the effects of salts on the speed of the reaction are summarized in Fig. 27. The action of the salts decreases in the order: $NiCl_2>MgCl_2>FeCl_3>HCl>AlCl_3>CrCl_3$; and $HgCl_2>CdCl_2>ZnCl_2$, where the action of the mercuric chloride is catalytic, and zinc chloride exerts a neutral salt effect. The subject was also discussed by M. Bobtelsky, and by M. Bobtelsky and D. Kaplan. L. L. de Koninck noticed that when potassium bromide is melted with a chromate, bromine is liberated.

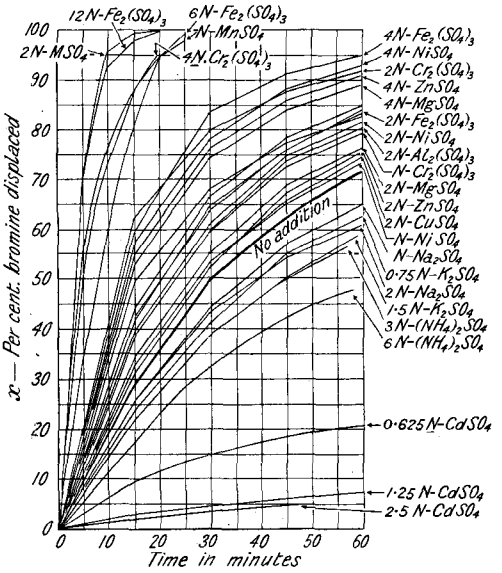


FIG. 27.—The Effect of Salts on the Reaction: $6HBr+2CrO_3=Cr_2O_3+3H_2O+3Br_2$.

H. Moissan found that dry **hydrogen iodide** has no action on chromium trioxide; and F. Penny, C. F. Mohr, E. Donath, and M. M. Richter observed that with boiling **hydriodic acid**, and iodides, iodine is set free. According to W. Ostwald, the reaction $2CrO_3+6HI=2Cr(OH)_3+3I_2$ is accelerated by the presence of free acids proportionally with the affinity constants of the acids. R. E. de Lury found that the velocity of oxidation of potassium iodide by potassium dichromate is proportional to the conc. of the dichromate, and to the square of the conc. of the acid employed. The temp. coeff. of the reaction is about 1·4. The presence of ferric salts strongly accelerates the reaction. The theory of R. Luther and co-workers is that the induction of the reaction between chromic acid and iodides by ferrous salts is due to the formation of quinquevalent chromium by the reaction between ferrous ions and sexivalent chromium ions, these then oxidizing other ferrous ions and also iodide ions. According to C. Wagner and W. Preiss, the equilibrium $Cr^{VI}+Fe^{II}\rightleftharpoons Cr^{V}+Fe^{III}$ is established very rapidly, and C. C. Benson, having shown that the oxidation of ferrous salts by chromic acid is proportional to the square of the conc. of the ferrous salt, said that the reaction between $Cr^{V}$-ions and $Fe^{\cdot\cdot}$-ions can primarily involve only one of the latter, somewhat as follows: $Cr^{V}+2Fe^{II}\rightarrow Cr^{III}+2Fe^{III}$. The reaction with the iodide ion also proceeds in two stages with hypoiodous acid as an intermediate product: $Cr^{V}+I^{I}+HO^{I}\rightarrow Cr^{III}+HIO$; and $HIO+H^{\cdot}+I'\rightarrow I_2+H_2O$. The values of the velocity cosntants indicate that there is a side reaction involving the splitting up of some $Cr^{V}$-ions possibly into $Cr^{III}$- and $Cr^{VI}$-ions. The reaction was also studied by K. Seubert and J. Carstens, K. Seubert and A. Henke, C. Wagner and W. Preiss, P. A. Meerburg, R. H. Clark, W. Manchot and R. Kraus, R. F. Beard and N. W. Taylor, W. Preiss, A. Schükareff, C. C. Benson, J. M. Bell, W. C. Bray, R. A. Gortner, R. Luther and T. F. Rutter, M. H. Golblum and L. Lew, M. Bobtelsky, and N. A. Orloff. W. B. Morehouse found the X-ray absorption of aq. soln. is greater

by 0·25 per cent. after than before the reaction: $K_2Cr_2O_7+12KI+14HCl=8KCl+2CrCl_3+3I_2+6KI+7H_2O$. N. Schiloff studied the catalytic action of chromate ions on the reaction between potassium bromate and potassium iodide. N. R. Dhar showed that the speed of the reaction between chromic acid and potassium iodide is increased in sunlight; and S. S. Bhatnagar and co-workers, that it is accelerated by a magnetic field. F. E. E. Germann and D. K. Shen studied the action of chromic acid on silver iodide photographic plates.

H. Moissan[3] found that when chromium trioxide is heated with **sulphur,** the mixture inflames, forming sulphur oxides and chromium sulphide. K. Brückner said that chromic oxide and a little sulphide are formed. J. B. Senderens observed that when the mixture is triturated in the cold, sulphur dioxide and a brown mush of chromic chromate and sulphate are formed—if water be present, the reaction does not occur in the cold. According to O. Harten, when **hydrogen sulphide** is passed over heated chromium trioxide, decomposition occurs with incandescence: $2CrO_3+6H_2S=Cr_2S_3+6H_2O+3S$. H. B. Dunnicliff and C. L. Soni studied the mechanism of the reaction, which they represented: $2H_2CrO_4+3H_2S=2Cr(OH)_3+2H_2O+3S$. H. Rose found that an aq. soln. of chromic acid reacts with hydrogen sulphide forming water, sulphur, and hydrated chromic oxide; aq. soln. of chromates mixed with acid become green when treated with hydrogen sulphide, and sulphur is precipitated; hot soln. are rapidly decomposed forming sulphuric acid. M. Traube found that dry **sulphur dioxide** does not react with dry chromium trioxide at 100°, and at 180°, sulphur trioxide and chromic chromate are slowly formed. P. Berthier said that aq. soln. of potassium dichromate and chromate are changed rapidly into a mixture of sulphate and dithionate; with the chromate soln., brown chromium hydroxide is first formed and then dissolved as more sulphur dioxide is passed into the soln. According to H. Bassett, when potassium dichromate, potassium chromate, or chromic acid is reduced by sulphurous acid, 94 to 95 per cent. of sulphate is formed together with 5 to 6 per cent. of dithionate, the amount of the latter produced being independent of the temp. The freshly reduced soln. do not give the reactions of chromium or of $SO_4$-ions, and appear to contain a compound $(KSO_4)Cr_2(SO_4)_2(KSO_3)$, or the corresponding acid, which slowly decomposes into chromic sulphate and potassium sulphite. If sulphuric acid or potassium sulphate is added to these soln., the reactions of $SO_4$ are not given by the resulting mixture. It seems possible that one mol of chromium sulphate may mask the reaction of as many as six mols of sulphuric acid. A. Skrabal said that if chromic acid be rapidly reduced by sulphur dioxide an unstable, green chromic salt is formed; and if slowly reduced with a feebly acid soln., a violet chromic salt is formed. H. Rose found that conc. **sulphuric acid** dissolves chromium trioxide forming, in the cold, a brownish-yellow soln. which gradually deposits crystals of chromium trioxide; if the soln. is heated to the evaporation temp. of sulphuric acid, oxygen is evolved and chromic chromate and sulphate are formed. A. Wesch observed that when warmed with sulphuric acid, chromium trioxide is decomposed more turbulently than potassium dichromate—oxygen is evolved but no ozone. C. Weltzien, and C. T. Kingzett observed that when conc. sulphuric acid and potassium dichromate are heated together, ozonized oxygen is evolved; J. C. G. de Marignac denied this. L. I. de N. Ilosva attributed the reaction to the presence of chlorine, not ozone, but R. Kraus found that when powdered potassium dichromate, free from chlorine is triturated with conc. sulphuric acid, ozone is formed. O. Brunck also observed a formation of ozone. A. W. Rakowsky and D. N. Tarassenkoff measured the solubility of chromium trioxide in sulphuric acid between 0° and 100°, and they said that the smooth curves with high concentrations of sulphur trioxide suggest the existence of only one solid phase. A. Schrötter, and P. A. Bolley observed the solubility of chromium trioxide in sulphuric acid respectively of sp. gr. 1·660 and 84·5 per cent.; and J. Fritzsche found it to be very soluble in sulphuric acid of sp. gr. 1·85. L. F. Gilbert and co-workers found the solubility expressed in molar percentages at 25° to be:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $SO_3$ . | 0 | 1·47 | 16·41 | 32·04 | 33·17 | 37·79 | 38·97 | 45·80 | 58·94 |
| $CrO_3$ . | 25·78 | 21·10 | 1·11 | 1·62 | 1·58 | 0·43 | 0·36 | 0·44 | 0·88 |
| Solid phase | $CrO_3$ | | | | $CrO_3.SO_3$ | | | $CrO_3.SO_3.H_2O$ | |

The results are plotted in Fig. 75, in connection with chromyl sulphate. The solubilities at 45° are :

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $SO_3$ | 5·25 | 16·73 | 22·01 | 31·05 | 33·55 | 34·67 | 37·07 | 42·26 | 45·67 |
| $CrO_3$ | 13·79 | 1·00 | 0·17 | 1·16 | 1·15 | 1·11 | 0·63 | 0·38 | 0·30 |
| Solid phase | $CrO_3$ | | | | $CrO_3.SO_3$ | | | | $CrO_3SO_3.H_2O$ |

The results of A. W. Rakowsky and D. N. Tarassenkoff between 0° and 100°, are plotted in Fig. 28. The hydrate $SO_3.2H_2O$ forms metastable mixed crystals with chromium trioxide. J. Fritzsch said that the trioxide is slightly soluble in a soln. of **potassium hydrosulphate.** According to O. Brunck, chromium trioxide and chromates are immediately reduced by **sodium hyposulphite** at ordinary temp. forming chromic oxide or chromic salts. A. Longi and L. Bonavia observed that in the reaction between chromium trioxide and **thiosulphates,** W. Diehl's equation : $4K_2Cr_2O_7 + 3Na_2S_2O_3 + 13H_2SO_4 = 3Na_2SO_4 + 4Cr_2(SO_4)_3 + 4K_2SO_4 + 13H_2O$ is not correct. On adding a mineral acid and potassium dichromate to a dil. soln. of sodium thiosulphate, A. Longi found that the reaction : $2H_2CrO_4 + 6H_2S_2O_3 = 3H_2S_4O_6 + 2Cr(OH)_3 + 2H_2O$, occurs ; small quantities of sulphuric acid are simultaneously formed in accordance with the secondary reaction : $3H_2S_4O_6 + 14H_2CrO_4 + 16H_2O = 12H_2SO_4 + 7Cr_2(OH)_6$. Hydrogen sulphide is also produced, and both sodium thiosulphate and tetrathionic acid give this gas when small quantities of an acid or a chromic salt are added to their soln. ; more hydrogen sulphide is obtained at high than at low temp., and tetrathionic acid is more stable than the thiosulphate, for sodium thiosulphate gives hydrogen sulphide when treated with hydrogen dioxide or acetic acid, or when carbon dioxide is passed through its hot soln. The reaction was studied by F. J. Faktor ; and G. Powarnin and M. Chitrin showed that in conc. soln., the oxidation proceeds most readily in the absence of an excess of acid—*i.e.* no more than 8H' per 2Cr. No more than 4·2 mols of thiosulphate per mol of potassium dichromate take part in the first stage of the reaction ; the proportion of sulphur separated increases with the conc. of the H'-ions ; in neutral soln. no sulphur is formed and the reaction proceeds : $2Cr_2O_7'' + S_2O_3'' = CrO_4'' + 2SO_3'' + 3CrO_2$. When the proportion of H'-ions is raised from 8 to 14 per 2Cr, the amount of thiosulphate which undergoes change is altered, and more sulphur is separated. This indicates that when the conc. of the H'-ions is low, tetrathionate is formed, and the tetrathionate is decomposed when the conc. of the H'-ions is high. H. Moissan observed that **selenium** reacts violently with the trioxide.

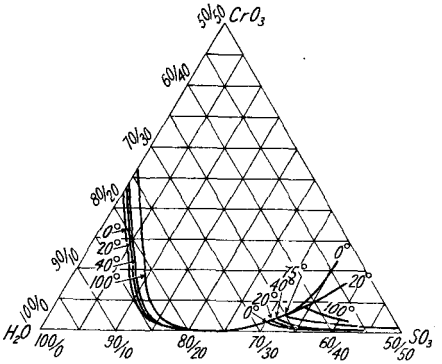


FIG. 28.—The Ternary System : $CrO_3$–$SO_3$–$H_2O$ between 0° and 100°.

H. Moissan [4] said that **nitrogen** has no action on chromium trioxide. O. Unverdorben, and R. Böttger showed that **ammonia** gas decomposes the dry trioxide with incandescence at ordinary temp. forming chromic oxide. M. Berthelot examined the heat of the reaction. E. C. Franklin said that the trioxide is slightly soluble in liquid ammonia. According to A. Rosenheim and F. Jacobsohn, liquid ammonia acts on chromium trioxide in a sealed tube at ordinary temp. forming a brown complex-chromium triamminotrioxide, $CrO_3.3NH_3$, or more probably ammonium imidochromate, $NH : CrO(O.NH_4)_2$—*vide* amido compounds, **8**. 49, 21.

For the action of aq. ammonia, *vide* the ammonium chromates. F. Ephraim observed that the trioxide reacts vigorously when triturated with **sodium amide.** T. Curtius and F. Schrader observed that **hydrazine** is decomposed explosively by chromates; U. Roberts and F. Roncali said that 2 mols of potassium dichromate develop 3 mols of nitrogen, while K. Seubert and J. Carstens represented the reaction: $H_2Cr_2O_7+N_2H_4=2CrO_2+3H_2O+N_2$—chromium dioxide is formed as an intermediate product. E. J. Cuy and W. C. Bray represented the reaction with hydrazine in acidic soln. by $3N_2H_5^{\cdot}+2Cr_2O_7''+13H^{\cdot}=3N_2+4Cr^{\cdot\cdot\cdot}+14H_2O$. E. Schweizer represented the reaction in aq. soln. with **nitric oxide** by: $2K_2Cr_2O_7+2NO=2KNO_3+K_2CrO_4+Cr_2O_3.CrO_3$. The reaction was also studied by H. Reinsch, and C. W. Eliot and F. H. Storer. P. Grouvelle, and F. Wöhler found that **nitrous acid** reduces chromium trioxide in aq. soln. H. Rose said that **nitric acid** does not change the chromic acid of the chromates, but in conc. soln. red fuming nitric acid reduces chromic acid to chromic oxide and brown chromic chromate. E. Zettnow said that chromic acid is insoluble in nitric acid of greater sp. gr. than 1·46; and R. Bunsen, in fuming nitric acid containing no nitrous oxides. S. A. Mumford and L. F. Gilbert found that the solubilities of chromic acid in nitric acid of different conc., when compositions are expressed in grams per 100 grms. of soln., are, at 25°,

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $HNO_3$ | 0 | 2·28 | 5·95 | 13·25 | 35·35 | 59·11 | 74·47 | 82·90 | 91·36 |
| $CrO_3$ | 62·85 | 60·31 | 56·47 | 48·10 | 25·54 | 4·88 | 0·27 | 0·06 | 8·29 |

there is a minimum at 0·06 per cent. $CrO_3$. At 45°, there is a minimum with 0·44 per cent. $CrO_3$:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $HNO_3$ | 0 | 2·05 | 5·58 | 19·53 | 50·69 | 73·81 | 81·55 | 91·83 | 98·06 |
| $CrO_3$ | 53·51 | 61·27 | 57·93 | 43·41 | 13·15 | 0·88 | 0·44 | 3·39 | 9·42 |

The minimum solubility occurs with nitric acid approximating $18N$-$HNO_3$, or $HNO_3.H_2O$. The curves are simple and continuous. The sp. gr. of the mixed soln. are only approximately additive. H. Moissan observed that **phosphorus** reacts explosively with molten chromium trioxide; and A. Oppenheim found that an aq. soln. of chromic acid at 200° is reduced by red phosphorus to chromic chromate. According to J. Jacobson, phosphorus dissolves in a soln. of chromic acid to form chromic phosphate. E. Kopp observed that a soln. of potassium dichromate when heated, or exposed to sunlight, is reduced by phosphorus. Observations on this subject were made by A. Stiassny, and J. W. Slater—*vide* phosphorus. According to G. Viard, the rate of the reaction between chromic acid and **phosphorous acid** can be represented by $dx/dt=k(a-x)^4$. The initial velocity varies according to a 1·4 power of the concentration. S. S. Bhatnagar and co-workers found that the reduction with phosphorous acid is accelerated by a magnetic field. A. D. Mitchell represented the reaction with **hypophosphorous acid** (*q.v.*): $H_3PO_2+Cr_2O_7''=H_3PO_3+Cr_2O_6''$; followed by $2H_3PO_2+Cr_2O_6''+8H^{\cdot}=2H_3PO_3+2Cr^{\cdot\cdot\cdot}+4H_2O$. *Vide infra*, for the phosphochromates formed by condensation with **phosphoric acid.** H. Schiff represented the reaction with **phosphorus pentachloride** by $CrO_3+PCl_5=CrO_2Cl_2+POCl_3$, and by a secondary reaction, chromic chloride is formed. P. Walden showed that chromium trioxide is virtually insoluble in **phosphoryl chloride.** H. Moissan found that **arsenic** reacts with chromium trioxide with incandescence, forming arsenide. According to C. Reichard, an aq. soln. of chromium trioxide is reduced by **arsenic trioxide;** and the reaction was studied by R. E. de Lury, and W. L. Miller. A. Skrabal showed that if the reaction proceeds slowly, violet chromic salt is formed, and if rapidly, a green salt—*vide* **9.** 51, 22, for the arsenic chromates formed by condensation with **arsenic acid.**

M. Berthelot [5] found that when heated with conc. chromic acid, **carbon** furnishes carbon dioxide and oxalic acid. E. B. Alekseevsky and A. P. Musakin studied adsorption of chromic acid by charcoal. J. Hargreaves and T. Robinson noted that alkali chromates are reduced to chromic oxide by **carbon monoxide,** and an alkali carbonate is formed. B. Neumann and C. Exssner studied the conversion of soln.

of sodium chromate to dichromate by **carbon dioxide** under press. H. E. Armstrong observed that with **carbon disulphide** at 180°, a little carbonyl sulphide is formed; and R. Böttger observed that heated chromium trioxide is reduced by carbon disulphide. I. Guareschi found that **cyanogen bromide** is decomposed by chromic acid, forming bromine, chromic oxide, carbon dioxide, and ammonia. K. Someya studied the electrometric titration of potassium dichromate and potassium ferrocyanide. E. Ludwig observed that **methane** is not attacked by chromium trioxide; while **ethylene** furnishes carbon dioxide, water, formic acid, probably acetic acid, and, according to M. Berthelot, some aldehyde. M. Berthelot also observed that with **acetylene,** a conc. soln. of chromic acid gives carbon dioxide and formic acid, while with dil. soln. some acetic acid is formed; **allylene** yields propionic and acetic acids, etc.; and **propylene,** propionic acid, acetone, etc. R. Fittig found that the side-chains of the **aromatic hydrocarbons** are oxidized to CO.OH groups by chromic acid or a mixture of sulphuric acid and potassium dichromate. According to A. Schafarik, commercial **benzene** inflames in contact with powdered chromium trioxide, but **petroleum,** rectified over sodium, shows scarcely any signs of action after some weeks' contact with chromium trioxide; R. Böttger observed that the heated trioxide is reduced by petroleum or **turpentine.** A. Gawalowsky said that while chromium trioxide and chromates oxidize **alcohol** to aldehyde, a highly purified aq. soln. of chromic acid does not act on alcohol, but it does so if a drop of sulphuric acid be added. J. M. Eder added that a soln. of ammonium dichromate in absolute alcohol decomposes more rapidly than a soln. in 50 per cent. alcohol. The reaction is favoured by light. E. J. Bowen and C. W. Bunn studied the photochemical oxidation of the alcohols—methyl, ethyl, *n*-propyl, and *iso*-propyl—by dichromates. H. Wienhaus observed that chromic esters can be obtained by shaking a soln. of an aromatic tertiary alcohol in light petroleum or carbon tetrachloride with an excess of chromium trioxide. Aromatic secondary alcohols were decomposed by treatment with chromic acid; thymol was coloured blue; and eugenol was oxidized without coloration. S. Takegami observed that colloidal chromic chromate, $Cr(CrO_4)_3$, is formed when alcohol is added to a soln. of chromic acid. E. Müller and co-workers also studied the reaction. B. V. Tronoff and co-workers studied the velocity of oxidation of alcohol; and D. S. Morton examined the photochemistry of the reaction. A. Schafarik said that chromium trioxide is soluble in dried **ether,** freed from alcohol. R. M. Isham and C. E. Vail said that when chromic acid is added to ether, a violent reaction takes place with evolution of acetaldehyde vapour and the separation of green chromic oxide. If the chromic acid is introduced into ether previously cooled to −10°, a yellow soln. is first produced, but oxidation begins almost immediately with the same results as those obtained at the ordinary temp. B. V. Tronoff studied the velocity of oxidation of ethers and **esters.** A. Naumann said that the trioxide is soluble in **acetone.** N. R. Dhar, and G. Ulrich and T. Schmidt studied the reducing action of **formic acid** on chromium trioxide. C. Wagner observed that the reaction with formic acid progresses in stages, $CrO_3 \rightarrow Cr^{V} \rightarrow Cr^{III}$; and if a manganous salt is present as negative catalyst, $CrO_3 \rightarrow Cr^{V} \rightarrow 2Cr^{II} + Cr^{III}$. The retarding action of manganous salts on the oxidation of formic or lactic acid by chromic oxide is ascribed to their promoting the transformation of the quinquevalent chromium into sexivalent and tervalent chromium. A. Pictet found that glacial **acetic acid** forms acetochromic acid, $HO.CrO_2.C_2H_3O_2$; and A. Pictet and P. Genequand could not prepare a similar compound with formic acid or with **valeric acid** because of their reducing action; but with **butyric acid,** butyrochromic acid, $HO.CrO_2.C_4H_7O_2$, is formed. The oxidation of **oxalic acid** by chromium trioxide was observed by H. Vohl, W. P. Jorissen and L. T. Reicher, B. K. Mukerji and co-workers, A. K. Bhattacharya and N. R. Dhar, H. Kunz-Krause and P. Manicke, N. R. Dhar, and M. Prud'homme. K. Jablczynsky deduced an equation for the reducing action of oxalic acid on the assumption that it occurs in three stages; $Cr^{VI} \rightarrow Cr^{V}$ (i), $Cr^{V} \rightarrow Cr^{IV}$ (ii), and $Cr^{IV} \rightarrow Cr^{III}$ (iii). The

velocity constants are respectively $k_1$=0·0344, $k_2$=0·1322, and $k_3$=0·0238. N. R. Dhar found the reaction is about four times as fast in tropical sunlight as in darkness. The reaction was also studied by A. K. Bhattacharya and N. R. Dhar. C. Wagner observed that if a soln. of chromic acid is added to a mixed soln. of potassium iodide and sodium hydrocarbonate, no free iodine is formed, but a reacting mixture of oxalic and chromic acids will liberate appreciable amounts of iodine from the iodide. It is therefore to be concluded that some active intermediate product is formed in the reaction between chromic acid and oxalic acid, and the same is true for the reaction between chromic acid and tartaric acid. This substance is so unstable that it can scarcely be hydrogen peroxide, or a compound, of the nature of percarbonic acid, and attempts to detect the formation of these substances have, in fact, been futile, nor is there any evidence in favour of the existence of chromic acid-oxalic acid complexes. In the reaction between chromic acid and lactic acid, however, the intermediate product is more stable, probably owing to the formation of a complex compound with the lactic acid. Intermediate products are also formed in the oxidation of oxalic, **lactic, tartaric, and thiocyanic acids** by chromic trioxide. Chromium trioxide decomposes tartaric acid, and **citric acid** as observed by W. P. Jorissen and L. T. Reicher, and W. G. Vannoy. A. K. Bhattacharya and N. R. Dhar studied the photochemical decomposition of citric, tartaric, and lactic acids by chromic acid. H. S. Fry found chromium trioxide to be soluble in **acetic anhydride ;** and that **acetyl chloride** dissolved in carbon tetrachloride forms chromyl chloride ; **acetyl bromide** forms chromyl bromide ; but **acetyl iodide** does not react. A. Naumann observed that chromium trioxide is soluble in **benzonitrile,** and in **methyl acetate ;** but is sparingly soluble in **ethyl acetate.** R. Böttger found that ethyl acetate, and **ethyl nitrate** reduce hot chromium trioxide to chromic oxide. M. Prud'homme showed that the oxidation of indigo is greatly accelerated by the presence of oxalic acid. The reducing action of **paper** was observed by A. Maus ; **wool,** by G. Ulrich and T. Schmidt ; **sugar,** by W. P. Jorissen and L. T. Reicher ; **vegetable products,** by J. Jacobson ; **gelatin,** by E. P. Wightman and S. E. Sheppard ; and **animal fibres,** by M. A. Ilinsky and D. I. Kodner. E. Goldberg found that the velocity of the reaction with **quinine** in light is proportional to the intensity of light ; only those rays are active which are absorbed ; Beer's law holds good ; and the temp. coeff. of the reaction is small. R. Luther and G. S. Forbes showed that the quinine is alone sensitive to the light so that the first stage of the reaction is the formation of sensitized quinine with a velocity proportional to the light absorption ; and the second stage is a reaction with the sensitized quinine with a velocity which is proportional to the conc. of the chromic and sulphuric acids. The reaction was studied by D. S. Morton. A. K. Bhattacharya and N. R. Dhar, and B. K. Mukerji and co-workers studied the reaction with quinine sulphate. L. Cohn, and A. Windhaus indicated the use of chromium trioxide in the oxidation of organic compounds in the laboratory, and A. N. Dey and N. R. Dhar studied the kinetics of the oxidation of organic acids by chromic acid. Chromic acid and soluble chromates give precipitates with basic dyes, but not so with the insoluble chromates.

According to P. Lebeau,[6] **silicon** is not attacked by chromium trioxide. R. Bunsen said that chromates heated before the blowpipe flame impart a green colour to beads from **borax**, or **microcosmic salt ;** and L. Möser and W. Eidmann, that **boron nitride** reduces the trioxide to a lower oxide. L. F. Gilbert studied the system $CrO_3$–$B_2O_3$–$H_2O$ at 25° and 45°. For the solubility of **boric acid** and chromic acid in grams per 100 grms. of soln., and the sp. gr., he found :

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 25° | $CrO_3$ | 62·40 | 59·90 | 43·80 | 33·05 | 18·07 | 9·42 | 4·90 |
| | $B_2O_3$ | 0·10 | 0·16 | 0·65 | 1·02 | 1·58 | 2·28 | 2·79 |
| | Sp. gr. | 1·699 | 1·657 | 1·420 | 1·296 | 1·156 | 1·086 | 1·052 |
| 45° | $CrO_3$ | 61·56 | 58·10 | 57·50 | 57·34 | 53·80 | 25·60 | 2·40 |
| | $B_2O_3$ | 0·90 | 0·92 | 0·87 | 0·12 | 0·85 | 2·33 | 4·76 |
| | Sp. gr. | 1·674 | 1·612 | 1·603 | 1·603 | 1·528 | 1·219 | 1·038 |

J. L. Gay Lussac and L. J. Thénard observed that **sodium** or **potassium** reacts with chromium trioxide with incandescence. R. G. van Name and D. U. Hill found that the values for the monomolecular velocity constant $k$, in $dx/dt=k(a-x)$, when **copper** dissolves in 0·015 molar soln. of chromium trioxide with 0·05, 0·25, 1·25, and 5·0 molar proportions of sulphuric acid, were, respectively, 5·58, 6·95, 5·34, and 2·072; **silver** and the 0·015 molar chromium trioxide with 0·25, and 5·0 molar $H_2SO_4$, gave the constants 4·31, and 1·23 respectively. The initial velocity of the dissolution of silver in chromic acid is greater than that which characterizes the normal process of dissolution. This indicates that the velocity depends on the physical state of the metal, and is not entirely determined by the process of diffusion. The reduction of chromic acid by copper was discussed by V. H. Veley,[7] E. Murmann, and F. Fischer. According to R. G. van Name and D. U. Hill, in the action of 0·015$M$-$CrO_3$ and 5·0$M$-$H_2SO_4$ on **tin,** the velocity constant was 2·74; with **nickel,** 2·67; while with **cadmium** and 0·015$M$-$CrO_3$ and 0·25, 1·25, and 5·0$M$-$H_2SO_4$, the velocity constants were, respectively, 7·02, 5·32, and 2·67; and with **iron** and 0·015$M$-$CrO_3$ with 0·25 and 5·0$M$-$H_2SO_4$, the velocity constants were, respectively, 11·68, and 4·20. H. Moissan found that **zinc** reduces chromium trioxide and chromates to chromic oxide or salts; iron also reacts with the evolution of much heat. E. Heyn and O. Bauer observed that iron dissolves in dil. chromic acid, and iron treated with a certain conc. of the chromic acid, may be partially protected from rusting. R. G. van Name and D. U. Hill studied the rate of dissolution of copper, silver, cadmium, tin, and nickel in chromic acid. J. F. John found that **manganese** dissolves in chromic acid. J. Jacobson observed that **mercury** reduces an aq. soln. of chromium trioxide; and also soln. of chromates and dichromates. A. Charriou studied the adsorption of chromic acid by **aluminium hydroxide.** According to A. Scheurer-Kestner, **stannous chloride** is oxidized by chromium trioxide: $6SnCl_2+4CrO_3=3SnCl_4+3SnO_2+2Cr_2O_3$; F. Penny found that dichromates are also reduced by stannous chloride. M. Neidle and J. C. Witt found that the stoichiometric relations in the reaction between stannous chloride and potassium dichromate are the same in the absence of acid as in its presence; when potassium dichromate is added in the theoretical quantity to a soln. of stannous chloride in the absence of acid, brownish- and greenish-blue, gelatinous masses are formed, which dissolve and form a clear, deep olive-green soln. when the whole of the dichromate has been added. These soln. appear red by transmitted light. Dialysis, and extraction with alcohol, showed that the soln. consists of potassium and chromium chlorides, together with colloidal soln. of hydrated stannic and chromic hydroxides. On dialysis a clear sol, of the approximate composition $6SnO_2:1Cr_2O_3$, is obtained, and this sol contains the whole of the tin and about one-half of the chromium used in the reaction. The course of the reaction is given by the equation: $2K_2Cr_2O_7+6SnCl_4+(6x+y+1)H_2O \rightleftharpoons 4KCl+6SnO_2.xH_2O+Cr_2O_3.yH_2O+2CrCl_3+2HCl$. R. Kraus studied the action of soln. of **uranous salts** and **molybdous salts** on chromium trioxide soln.; and K. Someya, soln. of **titanous salts.** A. Geuther represented the reaction with anhydrous **ferric chloride** by: $2FeCl_3+3CrO_3=Fe_2O_3+3CrO_2Cl_2$. S. Orlowsky found that, in alkaline soln., potassium dichromate oxidizes **manganous salts** to manganic: $K_2Cr_2O_7+6MnSO_4+10NH_4OH+7H_2O=2Cr(OH)_3+6Mn(OH)_3+K_2SO_4+5(NH_4)_2SO_4$, and the more conc. the alkali, the smaller the oxidation produced. The reaction was studied by R. Lang and co-workers. For the action on permanganates, *vide* permanganates. Chromium trioxide is reduced by **ferrous salts.** M. Neidle and J. C. Witt found that the stoichiometric relations in the reaction between potassium dichromate and ferrous sulphate are the same in the presence or absence of acid. In the absence of acid the reaction is instantaneous, except in very dil. soln. The reaction may be expressed by the equation: $3K_2Cr_2O_7+18FeSO_4+(x+6y)H_2O=3K_2SO_4+Cr_2O_3.xH_2O+2Cr_2(SO_4)_3+3Fe_2(SO_4)_3+6(Fe_2O_3.yH_2O)$. The colloidal chromic and ferric oxides are precipitated by the sulphate ion in the soln., and adsorb a

large quantity of ferric sulphate and smaller quantities of the other two sulphates. The electrometric titration of ferrous salts with potassium dichromate was studied by R. G. van Name and F. Fenwick, and E. Müller and H. Kogert. C. Rube observed that **potassium ferrocyanide** is converted into ferricyanide.

F. Penny, H. Schwarz, and J. Schabus found that a soln. of **ferrous sulphate** gives a yellowish-brown precipitate with chromates or dichromates, which ultimately dissolves and a green soln. of a chromic salt remains. C. C. Benson observed that the rate of oxidation of ferrous sulphate is proportional to the second power of the conc. of ferrous salt and of acid ; and approximately proportional to the 1·7 power of the conc. of the potassium dichromate. The presence of ferric salts retards the reaction. In the presence of iodide, the rate of oxidation of the ferrous salt is proportional to the conc. of the dichromate and ferrous sulphate, and to the third or fourth power of the conc. of the acid. Increasing the conc. of iodide causes at first a decrease and later an increase of the rate. The results are not in accord with the peroxide theory of W. Manchot, which assumes the primary product of oxidation of the ferrous sulphate to be a peroxide, which then reacts with the iodide and the remaining ferrous salt ; but they agree with the assumption that the iodide takes part in the reaction, and the two reactions are suggested as occurring together (i) between $Cr_2O_7''$, $FeI'$, $I'$, and $4H^{\cdot}$, and (ii) between $Cr_2O_7''$, $2Fe''$, and $2H^{\cdot}$. The reaction was discussed by W. L. Miller, and R. A. Gortner. The reaction between chromic acid and hydriodic acid in dil. soln. has been studied by N. Schiloff, R. Luther and N. Schiloff, and R. Luther and T. F. Rutter in the presence of hydriodic acid as acceptor, and vanadium salts as inductors. Bi-, ter-, and quadrivalent salts of vanadium are ultimately oxidized to quinquevalent vanadium. The inductor factor is 2, meaning that for one eq. of vanadium oxidized, two eq. of iodine are set free. Vanadic acid does not effect the rate of oxidation of hydriodic acid by chromic acid, and only acts comparatively slowly on hydriodic acid, so that the process is not greatly complicated by side reactions. With uranous sulphate as inductor, and a large excess of potassium iodide, the induction factor is 0·74. While W. Manchot supposed that the inductor is oxidized by chromic acid to a peroxide, R. Luther and T. F. Rutter assumed that the inductor reduces chromic acid to quinquevalent chromium, which is a more rapid oxidizing agent than the acid itself. Whereas W. Manchot's theory requires the formation of intermediate peroxides of very diverse formulæ, the assumption of the intermediate formation of quinquevalent chromium alone accounts for nearly all the reactions so far investigated. It is suggested that the reduction of chromic acid proceeds in the following stages $Cr^{VI} \rightarrow Cr^{V} \rightarrow Cr^{IV} \rightarrow Cr^{III}$, and that chromic acid contains sexivalent and not quadrivalent chromium as W. Manchot has suggested. N. R. Dhar studied some induced reactions, *e.g.* the action of chromic acid on the reduction of mercuric chloride by oxalic acid.

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## § 15. The Chromates. Monochromates

The normal chromates are to be regarded as salts of the dibasic **chromic acid,** or rather **metachromic acid,** $H_2CrO_4$ ; it is possible that the hypothetical **parachromic acid,** $H_4CrO_5$, is represented by some of the basic salts—$PbO.PbCrO_4$ ; and the hypothetical **orthochromic acid,** $HCr_6O_6$, represented by other basic salts—*e.g.* $2PbO.PbCrO_4$.

L. N. Vauquelin,[1] J. B. Richter, and H. Moser obtained what was regarded as **ammonium chromate,** $(NH_4)_2CrO_4$, by evaporating an aq. soln. of chromic acid mixed with an excess of ammonia. J. J. Pohl said that with the ammonia in large excess, yellow crystals of *ammonium oxychromate*, $(NH_4)_2O.4(NH_4)_2CrO_4$, are formed; which, according to J. Schabus, are monoclinic prisms with the axial ratio $a : b : c = 0{\cdot}7458 : 1 : 0{\cdot}4955$, and $\beta = 106° 15'$. C. F. Rammelsberg doubted whether this compound really exists; J. J. Pohl's analysis was imperfect—only the chromium was determined. E. Jäger and G. Krüss showed that when an aq. soln. of chromic acid is evaporated with ammonia, the salt is partially decomposed with evolution of ammonia, and a mixture of chromate and dichromate is always obtained; even when the soln. is evaporated at 50° to 60°, reddish-yellow crystals containing 59·19 per cent. of chromic oxide are obtained, and at ordinary temp., also, a mixture of the two salts is produced. According to Y. T. Gerasimoff, the salt cannot be conveniently prepared by double decomposition, but it can be made by neutralizing chromic acid with ammonia. Ammonium chromate can be prepared by treating chromic acid, free from sulphuric acid, with aq. ammonia of sp. gr. 0·9, adding ammonia and warming gently until the solid salt which separates is redissolved, and then placing the soln. in a freezing mixture. It crystallizes in long, golden needles. E. Maumené said that a conc. soln. of chromic acid or potassium dichromate neutralized by ammonia, deposits ammonium chromate in yellow, crystalline tufts, which resemble those of the potassium salt, but soon lose ammonia, and change into the dichromate. The salt is best crystallized by evaporating the slightly ammoniacal soln. over quicklime, and should be kept in sealed vessels. H. Hirzel obtained ammonium chromate by gradually adding chromyl chloride to an excess of aq. ammonia, and evaporating the soln. below 60°. The first crop of crystals is ammonium chromate; and the next crop, ammonium chloride. The salt was purified by recrystallization. Analyses by E. Kopp, S. Darby, and E. Jäger and G. Krüss agreed with the formula $(NH_4)_2CrO_4$. E. Maumené, L. N. Vauquelin, H. Moser, and E. Jäger and G. Krüss showed that when the aq. soln. of the salt is repeatedly evaporated, it is first converted into the dichromate, and then into a brown oxide. E. Jäger and G. Krüss could not prepare any basic salt like that reported by J. J. Pohl; nor did F. A. H. Schreinemakers observe the formation of any basic salt during his study of the ternary system: $CrO_3$–$NH_3$–$H_2O$, at 30°. The following is a selection from the solubility data for sat. soln.—concentrations are expressed in percentages:

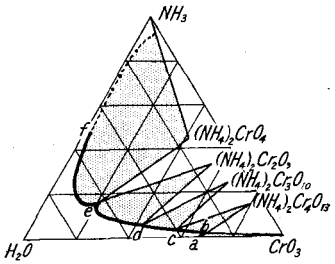


FIG. 29.—Equilibrium Diagram for the Ternary System: $CrO_3$–$NH_3$–$H_2O$ at 30°.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $CrO_3$ | 6·933 | 9·966 | 14·486 | 18·98 | 27·09 | 25·43 | 42·437 |
| $NH_3$ | 22·348 | 16·529 | 10·780 | 6·49 | 6·87 | 4·34 | 3·1483 |
| Solids | $(NH_4)_2CrO_4$ | | | | $(NH_4)_2Cr_2O_7$ | | |
| $CrO_3$ | 44·08 | 52·41 | 56·62 | 58·87 | 63·60 | 62·94 | 62·28 |
| $NH_3$ | 2·271 | 1·107 | 0·9496 | 0·6485 | 0·3991 | 0·2094 | — |
| Solids | $(\dot{N}H_4)_2Cr_3O_{10}$ | | | $(\dot{N}H_4)_2Cr_4O_{13}$ | | $CrO_3$ | |

The results are shown respectively in Fig. 29. The region above the line *abcdef* refers to unsaturated soln.; *ab* represents soln. in equilibrium with solid chromium trioxide; *bc*, with solid ammonium tetrachromate; *cd*, with solid trichromate; *de*, with solid dichromate; and *ef*, with solid monochromate. Ammonia was here selected as one of the components because $(NH_4)_2O$ is not stable.

According to E. Jäger and G. Krüss, the golden-yellow needles are monoclinic

prisms with the axial ratios $a : b : c = 1{\cdot}9603 : 1 : 2{\cdot}4452$, and $\beta = 64° 47'$. E. Herlinger studied the structure of the crystals. J. W. Retgers said that ammonium chromate is not isomorphous with the potassium chromate family. The other measurements of G. N. Wyrouboff made it appear as if the salt is dimorphous, like potassium chromate ; but more data are required to confirm these results ; however, he found that ammonium chromate forms an isomorphous series of solid soln. with anhydrous, rhombic sodium sulphate, and another series with anhydrous, monoclinic sodium sulphate. There is a gap between the two series, and hence, the salt exhibits what has been called a labile dimorphism. T. Ishikawa studied the system : $(NH_4)_2CrO_4$–$(NH_4)_2SO_4$–$K_2SO_4$–$K_2CrO_4$. S. Araki found that the solubility curve in the system : $(NH_4)_2CrO_4$–$(NH_4)_2SO_4$–$H_2O$ at 25° has two branches with two series of solid soln. No solid soln. occur with ammonium sulphate between 2·90 and 21·50 molar per cent.—*BC*, Fig. 30. He also studied the system : $(NH_4)_2CrO_4$–$K_2CrO_4$–$H_2O$. H. G. C. Schröder gave 1·866 for the sp. gr. of ammonium monochromate ; F. W. Clarke, 1·917 at 12° ; and E. Jäger and G. Krüss, 1·886, at 11°. K. F. Slotte found the sp. gr. of aq. soln. with 10·52, 19·75, and 28·04 per cent. of $(NH_4)_2CrO_4$ to be respectively 1·0633 at 13°, 1·1197 at 13·7°, and 1·1727 at 19·6° ; and the viscosity (water 100) respectively 108·3, 120·3, and 137·9 at 10° ; 85·2, 95·5, and 110·1 at 20° ; and 57·8, 66·1, and 76·9 at 40°. The sp. ht. of aq. soln. of a mol of ammonium chromate with $n$ mols of water was found by J. C. G. de Marignac to be 0·7967 for $n=25$ ; 0·8767 for $n=50$ ; 0·9304 for $n=100$ ; and 0·9630 for $n=200$. The subject was discussed by N. de Kolossowsky. F. Morges gave for the heat of neutralization : $(H_2CrO_{4aq.}, 2NH_4OH_{aq.}) = 22{\cdot}2$ Cals. at 12° ; and M. Berthelot, 24·42 Cals. at 19·5°. F. Morges also gave $(NH_4)_2Cr_2O_{7aq.}, 2NH_4OH_{aq.}) = 20{\cdot}4$ Cals. at 12°. P. Sabatier found −5·8 Cals. for the heat of soln. of a mol of ammonium chromate in 200 parts of water at 18°. The spectroscopic observations of D. Brewster, and J. H. Gladstone have been previously discussed. M. G. Mellon studied the colour of soln. of different concentration. I. Plotnikoff and M. Karshulin measured the absorption spectrum and the region of photochemical sensitivity for collodion films with methyl alcohol as acceptor. M. S. Sherrill found the eq. conductivity, $\lambda$ mho, corrected for hydrolysis, for $m$ grm.-equivalents of the salt per litre at 18°, to be .

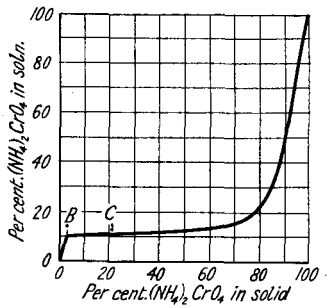


FIG. 30.—Solubility of Binary Mixtures: $(NH_4)_2CrO_4$–$(NH_4)_2SO_4$ at 25°.

| | | | | | |
|---|---|---|---|---|---|
| $m$ | 0·005 | 0·01 | 0·02 | 0·04 |
| $\lambda$ | 123·4 | 118·4 | 112·5 | 105·5 |

and C. Watkins and H. C. Jones gave for the molar conductivity, $\mu$ mho, of a mol of salt in $v$ litres,

| $v$ | 4 | 8 | 16 | 32 | 128 | 512 | 1024 |
|---|---|---|---|---|---|---|---|
| $\mu$ 0° | 99·8 | 109·3 | 117·8 | 126·9 | 144·0 | 154·1 | 152·4 |
| $\mu$ 15° | 146·0 | 159·7 | 173·9 | 187·9 | 214 | 227 | 227 |
| $\mu$ 25° | — | 193i9 | 213 | 230 | 263 | 280 | 279 |
| $\mu$ 35° | — | 230 | 282 | 274 | 312 | 333 | 333 |

The calculated percentage ionizations at 0° and 35° are :

| $v$ | 4 | 8 | 16 | 32 | 128 | 512 |
|---|---|---|---|---|---|---|
| 0° | 66·7 | 70·8 | 76·4 | 82·3 | 93·4 | 100·0 |
| 35° | — | 68·8 | 75·7 | 82·2 | 93·6 | 100·0 |

M. S. Sherrill calculated the hydrolysis of a 0·05 molar soln. at 18° to be 2·7 per cent. According to A. Naumann and O. Rücker, a not very exact distillation process

showed that the hydrolysis expressed in percentages of the ammonia content, for soln. containing $m$ gram-equivalents of salt per litre, was:

| $m$ | 1·0 | 0·4 | 0·1 | 0·025 | 0·0025 |
|---|---|---|---|---|---|
| Hydrolysis | 31·0 | 32·6 | 36·8 | 42·0 | 49·0 |

E. Jäger and G. Krüss said that ammonium chromate is not particularly stable in the dry state, and on exposure to air, it gradually turns reddish-yellow owing to the formation of the dichromate; it also decomposes in a dry atm., or when gently heated. A. Maus observed that decomposition occurs with glowing, when heated, and the green chromic oxide which remains is readily soluble in acids. W. C. Ball observed that when heated, it decomposes like the dichromate (*q.v.*). According to E. Maumené, ammonium chromate yields a brown oxide, $CrO_2$, when heated at 204°, identical with the oxide which was described by L. N. Vauquelin as precipitated on heating the aq. soln., although in all probability it is formed only on the superheated sides of the vessel. When the temp. is raised to 220° or 225°, explosive decomposition occurs, and the oxide CrO is formed, which, however, takes fire at once, and burns to the green oxide $Cr_2O_3$; it is probable that the compound $N_2H_4CrO_3$ is formed as an intermediate product. F. A. H. Schreinemakers found that 40·46 grms. of the salt dissolve in 100 grms. of water at 30°—*vide supra*. In consequence of hydrolysis, the soln., as noticed by L. N. Vauquelin, H. Moser, and E. Jäger and G. Krüss, reacts alkaline, and gradually loses ammonia. Consequently, as pointed out by E. Maumené, it should be crystallized from aq. soln. in an atm. of ammonia. M. Gröger observed that the aq. soln. containing the molar proportions $2NH_3 : CrO_3$ is orange coloured, not yellow. He therefore assumed that the soln. contains a large proportion of dichromate: $2(NH_4)_2CrO_4 \rightleftharpoons 2NH_3+H_2O+(NH_4)_2Cr_2O_7$. C. Paal and G. Brünjes found that in the presence of colloidal palladium, a soln. of ammonium chromate is reduced by hydrogen. W. Müller found that the vapour of carbon disulphide converts it into chromium sulphide and oxide. H. Stamm measured the solubility of the salt in aq. ammonia and found that soln. with 0, 1·818, and 3·436 mols of $NH_3$ per 100 grms. of water dissolve, respectively, 0·200, 0·066, and 0·043 mol of $(NH_4)_2CrO_4$. E. C. Franklin found that the salt is sparingly soluble in liquid ammonia; and A. Naumann, sparingly soluble in acetone.

G. C. Gmelin,[2] C. F. Rammelsberg, and L. Schulerud prepared **lithium chromate,** $Li_2CrO_4.2H_2O$, by evaporating an aq. soln. of lithium carbonate in chromic acid. J. W. Retgers said that if the soln. be evaporated at this temp., or if the salt be heated to 150°, the anhydrous salt is formed, and it consists of needle-like crystals probably isomorphous with anhydrous lithium sulphate. F. Mylius and R. Funk said that a soln. of the salt sat. at 18° contains 52·6 grms. of $Li_2CrO_4$ per 100 grms. of water; W. Kohlrausch said that 100 c.c. of soln. at 18° contain 85 grms. $Li_2CrO_4$; P. P. von Weimarn, 100 grms. of water at 20° dissolve 111 grms. of salt, and F. A. H. Schreinemakers said 99·94 grms. at 30°. The salt deposited from its aq. soln. is the *dihydrate*, $Li_2CrO_4.2H_2O$, as proved by the analyses of C. F. Rammelsberg, and L. Schulerud.

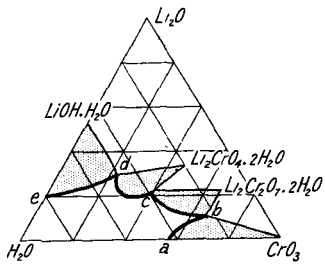


FIG. 31.—Equilibrium Diagram for the Ternary System: $Li_2O$–$CrO_3$–$H_2O$ at 30°.

F. A. H. Schreinemakers observed that the ternary system: $Li_2O$–$CrO_3$–$H_2O$, at 30°, contains the following percentage proportions of lithium oxide and chromium trioxide:

| $CrO_3$ | — | 22·51 | 37·50 | 38·55 | 43·40 | 49·60 | 67·73 | 63·26 | 62·28 |
|---|---|---|---|---|---|---|---|---|---|
| $Li_2O$ | 7·09 | 9·88 | 16·34 | 11·44 | 11·81 | 7·33 | 5·69 | 2·14 | — |
| Solids | $LiOH.H_2O$ | | $Li_2CrO_4.2H_2O$ | | $Li_2Cr_2O_7.2H_2O$ | | | $CrO_3$ | |

The results are summarized in Fig. 31: the curve *ab* refers to soln. in equilibrium

with solid chromium trioxide; *bc*, with solid $Li_2Cr_2O_7.2H_2O$; *cd*, with solid $Li_2CrO_4.2H_2O$; and *de*, with solid $LiOH.H_2O$. G. C. Gmelin said that lithium chromate furnishes orange-yellow, rhombic prisms, or dendritic masses, which, according to C. F. Rammelsberg, have the axial ratios $a : b : c = 0{\cdot}662 : 1 : 0{\cdot}466$. F. Mylius and J. von Wrochem found that the soln. sat. at 18°, has a sp. gr. 1·574; A. Heydweiller gave for the sp. gr. of gram-equivalent soln. at 18°/18°,

| | 0·0815*N*- | 0·1629*N*· | 0·4115*N*- | 0·823*N*· | 2·057*N*· | 4·115*N*· |
|---|---|---|---|---|---|---|
| Sp. gr. . . | 1·00458 | 1·00902 | 1·02052 | 1·04437 | 1·10746 | 1·20659 |

C. F. Rammelsberg said that the salt is deliquescent, but when confined over conc. sulphuric acid, it effloresces; and, added L. Schulerud, it loses its water of crystallization at 130°, and melts at a higher temp. P. P. von Weimarn added that when the molten mass is rapidly cooled, it furnishes a transparent glass. G. Tammann found that 4·63, 20·23, 41·93, and 59·09 grms. of lithium chromate in 100 grms. of water lower the vap. press. respectively 11·5, 53·6, 131·2, and 205·2 mm. A. Heydweiller found the indices of refraction of 0·1, 0·5, 1·0, and 4·0*N*-$Li_2CrO_4$ are respectively 1·33529, 1·34307, 1·35251, and 1·40612 for the *D*-line at 18°; and the eq. electrical conductivities, $\lambda$ mhos, of 0·0815, 0·4115, and 4·115*N*-soln. are respectively $\lambda = 76{\cdot}02$, 59·67, and 22·73 at 18°. C. Watkins and H. C. Jones gave for molar conductivity, $\mu$ mhos, for a mol of salt in $v$ litres of water,

| $v$ . . . | 8 | 16 | 32 | 128 | 512 | 1024 | 2048 |
|---|---|---|---|---|---|---|---|
| $\mu$ 0° . . | 80 | 88 | 96 | 108 | 113 | 115 | 122 |
| $\mu$ 15° . . | 120 | 132 | 146 | 165 | 175 | 177 | 179 |
| $\mu$ 25° . . | 149 | 164 | 181 | 206 | 129 | 220 | 223 |
| $\mu$ 35° . . | 180 | 200 | 219 | 252 | 265 | 267 | 268 |

The percentage ionizations at 0° and 35° are:

| $v$ . . | 8 | 16 | 32 | 128 | 512 | 1024 | 2048 |
|---|---|---|---|---|---|---|---|
| 0° . . | 65·4 | 72·4 | 78·7 | 89·0 | 93·2 | 94·7 | 100·0 |
| 35° . . | 67·2 | 74·5 | 81·7 | 94·0 | 99·0 | 99·5 | 100·0 |

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H. Traube said that complex **lithium potassium sulphatochromate,** $Li_2CrO_4.K_2SO_4$, furnishes hexagonal crystals. C. F. Rammelsberg prepared what he regarded as **ammonium lithium chromate,** $(NH_4)LiCrO_4.2H_2O$, in non-deliquescent crystals from a soln. of the component salts.

Methods indicated in connection with the extraction of chromium from chromite can be made to yield **sodium chromate,** $Na_2CrO_4$. H. Moser [3] obtained it by fusing chromite with sodium hydroxide and nitrate, and crystallizing from an aq. soln. of the cold cake; and H. Kopp, by fusing chromic oxide with sodium nitrate, etc. J. d'Ans and J. Löffler obtained the chromate amongst the products of the action of chromic oxide on sodium hydroxide. M. R. Nayer and co-workers found that sodium carbonate and chromic oxide readily interact to form chromate at temp. below 660°; the salt melts at 800° and remains undecomposed after prolonged heating at 1000°. Ferric oxide and, to a greater extent, calcium oxide, accelerate the formation of chromate in mixtures of sodium carbonate and chromic oxide by preventing the mass from fusing and thus allowing better access of air. H. Moser obtained sodium chromate by neutralizing a soln. of chromic acid with sodium carbonate; and S. W. Johnson, by saturating a soln. of potassium dichromate with sodium carbonate and crystallizing the liquid. The salt can be so obtained free from potassium salts. M. de K. Thompson and co-workers, and A. J. B. Jouve and A. Helbronner obtained sodium chromate by electrolyzing sodium hydroxide soln. with ferrochromium anodes. If the aq. soln. be evaporated above 30°, H. Kopp, and J. W. Retgers said that the anhydrous salt is obtained; H. Traube gave 60° to 70°. Actually, the transition temp. is near 68°, Fig. 33. T. W. Richards and G. L. Kelley gave 62·8°. H. Traube added that the *dihydrate*, $Na_2CrO_4.2H_2O$, reported by G. N. Wyrouboff, is the imperfectly-dried, anhydrous salt.

J. W. Retgers said that the anhydrous sodium chromate forms yellow, columnar

crystals, probably rhombic, and not isomorphous with sodium sulphate; H. Traube said that the two salts are isomorphous; and gave for the rhombic, bipyramidal crystals the axial ratios $a : b : c = 0{\cdot}4643 : 1 : 0{\cdot}7991$. The (010)-cleavage is perfect. J. Traube and W. von Behren studied the crystallization of the salt. E. Flach showed that sodium chromate and sulphate are completely miscible and isomorphous. The effect of the sulphate on the transition points of the chromate is illustrated by Fig. 32. C. Leenhardt studied the speed of crystallization of the hydrates.

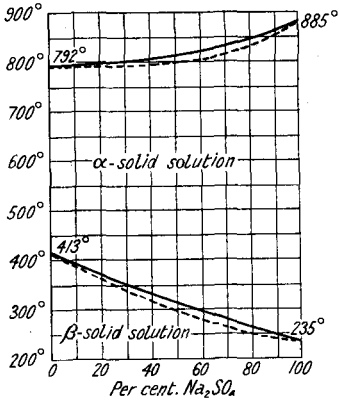



FIG. 32.—Effect of Sodium Sulphate on the Freezing and Transition Points of Sodium Chromate.

The existence of three hydrates has been established. F. W. Clarke gave 2·710 to 2·736 for the sp. gr.; and I. Traube added that the drop weight of the salt, at its m.p., is 328·2. The *tetrahydrate*, $Na_2CrO_4.4H_2O$, was prepared by D. Gernez by evaporating a supersaturated soln. of the decahydrate, or by contact of the soln. with the anhydrous salt. H. Traube obtained it from a conc soln. at 50°; and G. N. Wyrouboff, at 25° to 29°. J. Zehenter neutralized a soln. of potassium dichromate with sodium carbonate, and crystallized the mother-liquor after the separation of the $3K_2CrO_4.Na_2CrO_4$. The sulphur-yellow, acicular crystals were found by H. Traube to be monoclinic prisms with the axial ratios $a : b : c = 1{\cdot}1112 : 1 : 1{\cdot}0624$. E. Herlinger studied the structure of the crystals. T. W. Richards and W. B. Meldrum observed the formation of isomorphous mixtures of $Na_2SO_4.4H_2O$ and $Na_2CrO_4.4H_2O$. L. Delhaye measured the optical properties of the monoclinic crystals of the tetrahydrate prepared by allowing a soln. of sodium chromate, sat. at 50°, to cool to about 27°, filtering, and keeping for several days with occasional shaking. He gave for the optic axial angle $2V = 30°\ 50'$ for $\lambda = 462\mu\mu$: 29° 52′ for $\lambda = 502\mu\mu$; 25° 33′ for $\lambda = 536\mu\mu$; 21° 49′ for $\lambda = 563\mu\mu$; and 16° 56′ for $\lambda = 582\mu\mu$; and for the indices of refraction,

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\lambda$ | 535 | 573 | 589 | 600 | 625 | 650 | 670$\mu\mu$ |
| $\alpha$ | 1·576 | 1·566 | 1·561 | 1·559 | 1·551 | 1·545 | 1·536 |
| $\beta$ | 1·471 | 1·457 | 1·447 | 1·440 | 1·383 | 1·291 | 1·285 |
| $\gamma$ | 1·342 | 1·328 | 1·321 | 1·317 | 1·308 | 1·297 | 1·221 |

G. N. Wyrouboff gave for the optic axial angle $2E = 16°\ 10'$ for red-light, and 36° 22′ for green-light; he also said that the salt is somewhat deliquescent, and loses 2 mols. of water at 110°, and the rest at 250°; while H. Traube said that the salt loses water if allowed to stand in air for some time, and all the water is expelled at 150°. F. Mylius and R. Funk gave for the percentage solubility of the tetrahydrate—stable between 25·9° and 68°, Fig. 33—

| | | | | |
|---|---|---|---|---|
| | 25·6° | 36·0° | | |
| $S$ | 46·08 | 47·98 | | |
| | 45·0° | 54·5° | 65·0° | |
| $S$ | 50·20 | 52·28 | 55·23 | |

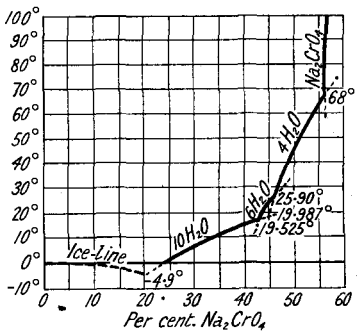



FIG. 33.—Solubility Curve of Sodium Chromate.

H. Salkowsky obtained the *hexahydrate*, $Na_2CrO_4.6H_2O$, accidentally from the mother-liquors of a soln. out of which the salt, $Na_2CrO_4.4H_2O$, had been crystallized. It crystallized in triclinic plates, and further crops were obtained by seeding sat. soln. of sodium chromate with it.

The percentage solubility of the hexahydrate—stable between 19·526° and 25·90°, Fig. 33—is:

| | 17·7° | 19·2° | 21·2° | 24·7° | 26·6° |
|---|---|---|---|---|---|
| *S* | 43·65 | 44·12 | 44·64 | 45·75 | 46·28 |

The *decahydrate*, $Na_2CrO_4.10H_2O$, is the salt obtained when the soln. is crystallized at ordinary temp., and it is the form stable below 19·526°. The crystals obtained by H. Moser, and J. F. John were lemon-yellow, and had a rough, metallic taste, and alkaline reaction. H. J. Brooke found that the monoclinic crystals, isomorphous with decahydrated sodium sulphate, have the axial ratios $a:b:c=1{\cdot}1127:1:1{\cdot}2133$, and $\beta=107°\ 43'$; V. Rosiczky gave $1{\cdot}1038:1:1{\cdot}2351$, and $\beta=72°\ 28°$. I. Takeuchi thought that a definite sodium trisulphatochromate, $2Na_2SO_4.Na_2CrO_4.30H_2O$, was formed at 25°, but Y. Osaka and R. Yoshida found that it is not a definite compound. Rather is it a solid soln. No solid soln. exists at 33°. At 28° and 31°, the chromate exists as the tetrahydrate and its solubility in the sulphate as the decahydrate decreases as the temp. rises, the molar fraction being 0·16 at 28° and 0·04 at 31°. G. N. Wyrouboff gave for the optical axial angle of the decahydrated chromate $2Y=83°\ 56'$ for red-light, and 82° 20′ for green-light. F. W. Clarke gave 1·483 for the sp. gr., and V. Rosiczky, 1·526. H. Kopp said that the crystals melt by the heat of the hand; S. W. Johnson gave 20°–21° for the m.p.; W. A. Tilden, and M. Berthelot gave 23°; J. L. R. Morgan and H. K. Benson, 19·92°; and F. Mylius and R. Funk said that there is a congruent m.p. at 21°. The m.p. lies in the region of instability of the hydrate since at 19·525°, there is a transformation into the hexahydrate with partial melting. T. W. Richards and G. L. Kelley suggested this incongruent m.p. as a fixed point in thermometry. G. Tammann found that the transition temp., $\theta$, for $Na_2CrO_4.10H_2O \rightleftharpoons Na_2CrO_4.6H_2O + 4H_2O$, is lowered by an increase of press. $p$ kgrms. per sq. cm., so that:

| | | | | | | |
|---|---|---|---|---|---|---|
| $p$ | 1 | 400 | 600 | 1000 | 2300 | 3050 |
| $\theta$ | 19·60° | 18·50° | 17·50° | 14·90° | 7·00° | 0·00° |
| $dp/\theta$ | 350 | 200 | 150 | 165 | 110 | |

DropBooks

This agrees with R. Hollmann's observations that the decahydrate contracts on fusion 0·010 c.c. per gram of salt. H. J. Brooke, and T. Thomson said that the crystals effloresce very rapidly in cold, dry air; and, added H. Moser, they become moist only in a damp. atm. H. Lescoeur found that the vap. press. of the sat. soln. is 10·6 mm. at 20° so that if the partial press. of the water-vapour in atm. air exceeds this, the salt will be deliquescent. F. Mylius and R. Funk found the percentage solubility of the decahydrate—stable below 19·256°—is:

| | 0° | 10·0° | 18·5° | 19·5° | 21·0° |
|---|---|---|---|---|---|
| *S* | 24·04 | 33·41 | 41·65 | 44·78 | 47·40 |

Observations on the solubility were made by F. Kohlrausch, F. Mylius and R. Funk, I. Takeuchi, and H. Salowsky. T. W. Richards and co-workers gave for the transition point between the decahydrate and the hexahydrate 19·525° to 19·63° with 44·2 per cent. $Na_2CrO_4$; T. W. Richards and R. C. Wells, 26·6°; T. W. Richards and G. L. Kelley gave 25·90° and H. Salkowsky 26·6° with 46·3 per cent. $Na_2CrO_4$ for the transition point between the hexahydrate and the tetrahydrate; and F. Mylius and R. Funk, about 68° with 55·2 per cent. $Na_2CrO_4$ for the transition temp. between the tetrahydrate and the anhydrous salt. J. Zeltner gave −4·9 for the eutectic temp. between ice and the decahydrate. The percentage solubilities can be summarized:

| | 0° | 10° | 19·525° | 21·2° | 25·90° | 40° | 68° | 80° | 100° |
|---|---|---|---|---|---|---|---|---|---|
| *S* | 24·1 | 33·4 | 44·2 | 44·6 | 46·3 | 49·0 | 55·2 | 55·3 | 55·8 |
| | $Na_2CrO_4.10H_2O$ | | | $Na_2CrO_4.6H_2O$ | | $Na_2CrO_4.4H_2O$ | | $Na_2CrO_4$ | |

The results are plotted in Fig. 34. There is a metastable region; F. Mylius and R. Funk gave for the solubility in this region 47·4 per cent. $Na_2CrO_4$ at 21° with

the decahydrate as solid phase ; and the transition point 19·987° for the decahydrate and tetrahydrate. E. W. Washburn and E. R. Smith gave 19·51 for the transition temp. F. A. H. Schreinemakers observed that in the ternary system : $Na_2O$–$CrO_3$.$H_2O$ at 30°, when concentrations are expressed in percentages,

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $CrO_3$ | 0 | 2·0 | 10·21 | 10·22 | 10·74 | 19·26 | 28·82 | 48·70 |
| $Na_2O$ | 42·0 | 41·44 | 29·70 | 29·39 | 25·55 | 22·98 | 17·88 | 16·49 |
| Solids | $NaOH.H_2O$ | | $Na_2CrO_4$ | | $Na_4CrO_5.13H_2O$ | | $Na_2CrO_4.4H_2O$ | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $CrO_3$ | 48·70 | 55·09 | 66·13 | 67·37 | 68·46 | 66·88 | 65·72 | 64·48 |
| $Na_2O$ | 16·49 | 14·44 | 13·70 | 12·50 | 10·95 | 9·85 | 6·31 | 4·51 |
| Solids | $Na_2Cr_2O_7.2H_2O$ | | $Na_2Cr_3O_{10}.H_2O$ | | $Na_2Cr_4O_{15}.4H_2O$ | | $CrO_3$ | |

The solubility curve *ab* refers to the solid phase chromic acid; *bc*, to $Na_2Cr_4O_{13}.4H_2O$ ; *cd*, to $Na_2Cr_3O_{10}.H_2O$ ; *de*, to $Na_2Cr_2O_7.2H_2O$ ; *ef*, to $Na_2CrO_4.4H_2O$ ; *fg*, to $Na_4CrO_5.13H_2O$ ; *gh*, to $Na_2CrO_4$ ; and *hi*, to $NaOH.H_2O$. The basic salt, **sodium oxychromate,** $Na_4CrO_5.13H_2O$, or $Na_2O.Na_2CrO_4.13H_2O$, was obtained by F. Mylius and R. Funk from an aq. soln. of chromium trioxide sat. with sodium hydroxide. The pale-yellow crystals melt at 50° with the separation of sodium chromate. The

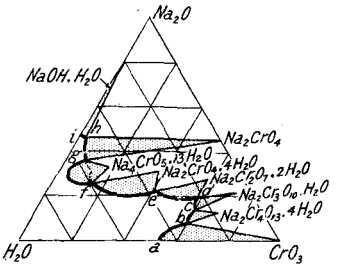



FIG. 34.—Equilibrium Diagram for the Ternary System : $Na_2O$–$CrO_3$–$H_2O$ at 30°.

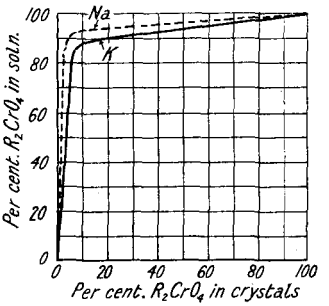



FIG. 35. — Crystallization of Mixed Solutions of Alkali Chromates and Sulphates.

aq. soln. saturated at 18° contains 37·5 per cent. of the anhydrous salt, and has a sp. gr. 1·446 ; and in soln. the salt is probably hydrolyzed. F. A. H. Schreinemakers said that it dissolves undecomposed in water, and the aq. soln. at 30° has 41·3 per cent. of the salt. F. Mylius and R. Funk gave for the percentage solubility :

| | 0° | 10° | 20·5° | 27·7° | 35° | 37° |
|---|---|---|---|---|---|---|
| *S* | 33·87 | 35·58 | 38·05 | 40·09 | 44·09 | 45·13 |

E. Flach studied the equilibrium between mixed soln. of sodium chromate and sulphate at 70° and the results are summarized in Fig. 35. With soln. containing 22, 62, 82, 91·5, and 96·5 per cent. of $Na_2CrO_4$, the separated crystals had, respectively, 0·21, 1·79, 3·45, 10·99, and 62·91 per cent. $Na_2CrO_4$ ; 99·16, 96·14, 94·58, 84·43, and 31·50 per cent. $Na_2SO_4$ ; and 0·63, 2·07, 1·99, 4·58, and 5·59 per cent. of water.

F. Mylius and R. Funk gave 1·409 for the sp. gr. of a soln. sat. at 18° ; A. Heydweiller, for soln. with 0·0533, 0·1066, 1·066, and 2·132 mols $Na_2CrO_4$ per litre at 18°, respectively 1·0077, 1·0152, 1·1442, and 1·2758 ; and H. C. Jones and H. P. Bassett, for soln. at 18°,

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $Na_2CrO_4$ | 0·81 | 1·60 | 3·15 | 6·14 | 8·98 | 11·69 | 14·28 per cent. |
| Sp. gr. | 1·0075 | 1·0152 | 1·0287 | 1·0561 | 1·0834 | 1·1100 | 1·1366 „ |

K. F. Slotte found the sp. gr. of aq. soln. containing 5·76, 10·62, and 14·81 per cent. sodium chromate to be respectively 1·0576 at 17·4°/4°, 1·1125 at 17·1°/4°, and

1·1604 at 20·7°/4°; and the viscosities (water 100), respectively at 10°, 117, 140·9, and 174; at 20°, 90·8, 108·3, and 132·5; at 30°, 72·8, 86·6, and 105·5; and at 40°, 59·8, 71·3, 85·9. J. L. R. Morgan and E. Schramm gave for the surface tension $\theta$ dynes per cm.:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $Na_2CrO_4$ | 4·45 | 12·67 | 24·05 | 34·91 | 45·25 | 49·81 | 53·13 per cent. |
| $\theta$ | 71·64 | 73·35 | 76·48 | 81·52 | 89·73 | 95·36 | 97·46 ,, |

For the observations of L. J. Simon on the viscosity of the soln. *vide infra*, potassium chromate. J. J. Coleman found that normal soln. of sodium molybdate, chromate, and tungstate diffused so that respectively 28, 25, and 17 per cent. rose 75 mm. in 30 days at 12·5°. J. C. G. de Marignac found for the sp. ht. between 21° and 52°, for soln. with 25, 50, 100, and 200 mols of water per mol of $Na_2CrO_4$, respectively 0·7810, 0·8560, 0·9134, and 0·9511. The subject was discussed by N. de Kolossowsky. G. Tamman observed the lowering of the vap. press. for soln. with 7·50, 30·88, 47·19, and 72·43 grms. of $Na_2CrO_4$ per 100 grms. of water, respectively 13·3, 61·6, 102·2, and 159·3 mm. of mercury—*vide supra*, for H. Lescoeur's observation. H. C. Jones and H. P. Bassett found the lowering of the f.p. for soln. with 0·1, 0·3, 0·6, and 1·0 mols of $Na_2CrO_4$ per litre to be respectively 0·450°, 1·230°, 2·345°, and 3·800°. F. Morges gave for the heat of neutralization of aq. soln. $(H_2CrO_4,2NaOH)$ =23·67 Cals. at 18°; J. Thomsen, $(H_2CrO_4(400\ aq.),2NaOH(400\ aq.))$=24·72 Cals., or, according to M. Berthelot, 28·72—30($\theta$—18) Cals. at $\theta$°; and $2H_2CrO_4(800\ aq.)+8NaOH(1600\ aq.)\rightarrow 2Na_2CrO_4\ aq.+4NaOH\ aq.$+50·328 Cals. at 18°. W. G. Mixter gave for the heat of formation: $Cr+3Na_2O_2=Na_2CrO_4+2Na_2O$+158·8 Cals.; $Cr_2O_{3cryst.}+3Na_2O_2=2Na_2CrO_4+Na_2O$+108·0 Cals.; and $(CrO_3,Na_2O)$=77·0 Cals. M. Berthelot found for the heat of soln., $Na_2CrO_4$ with 360 to 720 mols of water, 2·2 Cals. at 10·5°; $Na_2CrO_4.4H_2O$ with 650 mols of water, —7·6 Cals. at 11°; and $Na_2CrO_4.10H_2O$ with 760 mols of water, —15·8 Cals. at 10·5°. Accordingly, the heat of hydration is $(Na_2CrO_{4solid},10H_2O_{liquid})$=18·0 Cals. at 10·5°; and the heat of fusion of the decahydrate is —12·3 Cals. at 10·5°, and —13·4° Cals. at 23°. A. Heydweiller found the eq. conductivity, $\lambda$ mhos, at 18° for 0·1066*N*-, 0·533*N*-, 1·066*N*-, and 4·264*N*-soln. to be, respectively, 81·84, 65·73, 56·96, and 29·05. R. Lenz, and H. C. Jones and H. P. Bassett made some observations on this subject, and C. Watkins and H. C. Jones gave for the mol. conductivity, $\mu$ mhos, for a mol of salt in $v$ litres of water:

| $v$ | 4 | 8 | 16 | 32 | 128 | 512 | 1024 |
|---|---|---|---|---|---|---|---|
| $\mu$ 0° | 74·76 | 83·56 | 90·74 | 98·16 | 110·40 | 118·32 | 114·60 |
| $\mu$ 15° | 113·4 | 125·3 | 137·8 | 148·6 | 168·4 | 176·2 | 173·6 |
| $\mu$ 25° | — | 156·5 | 171·3 | 185·1 | 206·7 | 219·5 | 216·9 |
| $\mu$ 35° | — | 187·9 | 207·6 | 224·3 | 252·2 | 270·1 | 262·3 |

The percentage ionizations at 0° and 35° are:

| $v$ | 4 | 8 | 16 | 32 | 128 | 512 |
|---|---|---|---|---|---|---|
| 0° | 63·2 | 70·6 | 76·7 | 82·9 | 93·3 | 100·0 |
| 35° | — | 69·6 | 76·8 | 83·0 | 93·4 | 100·0 |

A. Berthoud observed no maximum in the conductivity curve. P. Düllberg studied the electrometric titration with hydrochloric acid. For the electrolysis of soln. of the chromate, *vide infra*, sodium dichromate. H. Ollivier studied the paramagnetism of the salt. H. Stamm measured the solubility of the salt in aq. ammonia, and found that soln. with 0 and 3·3079 mols $NH_3$ per 100 grms. of water dissolve 0·3595 and 0·1147 mol $Na_2CrO_4$, respectively. B. Neumann and C. Exssner studied the conversion of sodium chromate to dichromate on aq. soln. by carbon dioxide under press. J. F. John, and H. Moser said that the decahydrate is sparingly soluble in alcohol; C. A. L. de Bruyn found 100 grms. of absolute methyl alcohol dissolve 0·345 grm. of $Na_2CrO_4$ at 25°; and A. Naumann observed the salt to be insoluble in acetone. F. E. Brown and J. E. Snyder observed no reaction with boiling vanadium oxytrichloride and anhydrous sodium chromate.

L. Kahlenberg and W. J. Trautmann observed no reaction when the chromate is mixed with silicon and heated in a hard glass tube by a bunsen burner, but a strong reaction occurs when heated by a Méker burner. J. Zehenter precipitated **ammonium sodium chromate,** $(NH_4)NaCrO_4.2H_2O$, by adding alcohol to a mixed soln. of ammonium chromate and sodium carbonate; and G. N. Wyrouboff, from a mixed soln. of ammonium and sodium chromates. The rhombic, prismatic crystals are said to be isomorphous with the corresponding sulphate, the axial ratios are $a : b : c = 0{\cdot}4780 : 1 : 0{\cdot}8046$; the optical character is negative; and the optic axial angles for red and green light respectively are $2H_a = 93°\ 15'$ and $80°\ 15'$; $2H_0 = 108°\ 0'$ and $129°\ 30'$; and $2V = 83°\ 52'$ and $70°\ 56'$. According to J. Zehenter, the sp. gr. is 1·842 at 15°. The salt decomposes between 150° and 180° with the evolution of water and ammonia. The aq. soln. made just turbid with alcohol decomposes in light.

According to A. Raimondi,[4] the yellow mineral **tarapacaite** from the province of Tarapaca, Chili, occurs in the midst of the variety of soda-nitre called *caliche azufrado*. It is essentially a **potassium chromate,** $K_2CrO_4$, mixed with a little sodium chloride, nitrate, and sulphate, and potassium sulphate. I. Domeyko also observed its occurrence in the desert of Atacama, Chili. The preparation of potassium chromate has been discussed in connection with the extraction of chromium. T. Thomson, and J. von Liebig and F. Wöhler obtained it from the soln. obtained by neutralizing potassium dichromate with the carbonate. J. von Liebig and F. Wöhler converted chromic oxide into chromate by ignition with potassium chlorate; and V. Kletzinsky, fused potassium dichromate with the nitrate. N. J. Berlin purified the chromate by treating a soln. of the dichromate with a soln. of barium chromate in chromic acid; evaporated to dryness a mixture of the filtrate with an excess of potassium carbonate; and crystallized the product from aq. soln. until it was nearly free from alkali carbonate; digested the aq. soln. with silver chromate; and crystallized and recrystallized the chromate from the filtrate by spontaneous evaporation.

No hydrates are formed under ordinary conditions. Observations on the solubility of potassium chromate were made by T. Thomson, A. Michel and L. Krafft, H. Moser, M. Alluard, A. E. Nordenskjöld and G. Lindström, A. Étard, C. von Hauer, W. Kohlrausch, P. Kremers, M. Amadori, H. Schiff, K. F. Slotte, I. Koppel and E. Blumenthal, F. Flöttmann, and F. A. H. Schreinemakers. The general results show that the percentage solubility, $S$, is:

| | −11·33° | −5·75° | 0° | 10° | 20° | 40° | 60° | 80° | 100° | 105·8° |
|---|---|---|---|---|---|---|---|---|---|---|
| $S$ | 23·1 | 36·6 | 36·7 | 37·9 | 38·6 | 40·1 | 42·1 | 42·9 | 44·2 | 47·0 |

F. Flöttmann found the solubility at 15°, 20°, and 25° to be 2·725, 2·764, and 2·799 mols per litre, or 38·49, 38·94, and 39·38 per cent., respectively. The eutectic temp., ice and $K_2CrO_4$ is, according to L. C. de Coppet, −11·30° with 36·6 per cent. of salt; according to F. Guthrie, −11·00° and 36·3 per cent. of salt; and, according to I. Koppel and E. Blumenthal, at −11·70 and 35·3 per cent. of salt.

E. H. Riesenfeld and A. Wesch treated a conc. aq. soln. of $K_5[(CrO_4)_2Cy_5).5H_2O$ with alcohol; a red oil is precipitated. This is separated and covered with alcohol, and allowed to stand for some days in a calcium chloride desiccator, and purified by recrystallization. The analysis agrees with the *tetrahydrate*, $K_2CrO_4.4H_2O$. The pale yellow prisms gradually lose water, and they are slightly hygroscopic. The aq. soln. is neutral, and it is darker than that of ordinary potassium chromate, and paler than the dichromate.

The ternary system: $K_2O$–$CrO_3$–$H_2O$ at 30° was studied by F. A. H. Schreinemakers, who found for the percentage solubilities:

| $CrO_3$ | 0 | 0·18 | 5·6 | 20·67 | 10·43 | 46·46 |
|---|---|---|---|---|---|---|
| $K_2O$ | 47 | 34·6 | 20·58 | 19·17 | 4·91 | 3·25 |
| Solids | | $KOH.2H_2O$ | | $K_2CrO_4$ | | $K_2Cr_2O_7$ |

| $CrO_3$ | 44·46 | 47·65 | 49·73 | 55·83 | 63·14 | 62·28 |
|---|---|---|---|---|---|---|
| $K_2O$ | 3·25 | 2·67 | 2·25 | 0·87 | 0·56 | — |
| Solids | | $K_2Cr_3O_{10}$ | | $K_2Cr_4O_{13}$ | | $CrO_3$ |

The results are plotted in Fig. 36; where the solubility curve *ab* has the solid phase $CrO_3$; *bc*, potassium tetrachromate; *cd*, trichromate; *de*, dichromate; *ef*, chromate; and *fg*, $KOH.2H_2O$. I. Koppel and E. Blumenthal's results at 0°, 30°, and 60° are summarized in Figs. 37, 38, and 39. As before, *ab* represents the region when the solid phase is $CrO_3$; *bc*, $K_2Cr_4O_{13}$; *cd*, $K_2Cr_3O_{10}$; *de*, $K_2Cr_2O_7$; *ef*, $K_2CrO_4$; and *fg*, $KOH.4H_2O$ at 0°; $KOH.2H_2O$ at 30°; and $KOH.H_2O$ at 60°. The results are collected together in the model, Fig. 41, where the area $gg_0f_0f$ refers to the hydrates of potassium hydroxide; $f_0fee_0$, to $K_2CrO_4$; $e_0edd_0$, to $K_2Cr_2O_7$; $d_0dcc_0$, to $K_2Cr_3O_{10}$; $c_0cbb_0$, to $K_2Cr_4O_{13}$; $b_0baa_0$, to $CrO_3$; $gfedcbaO$, to ice; and the area $g_0f_0E'_0e_0E_0d_0c_0b_0a_0(O_0)$, to the region where the vap. press. is 760°. $E'E'_0$ and $EE_0$ are eutectic lines. The b.p. for $f_0$ is 109°; $E'_0$, 105° 8°; $e_0$, 106·8°; $E_0$, 104·8°; $d_0$, 114·0°; and $a_0$, 127·0°. W. Herz

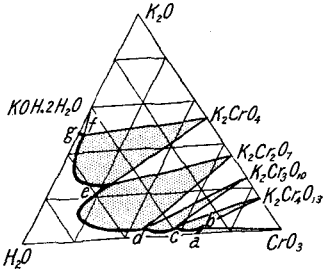
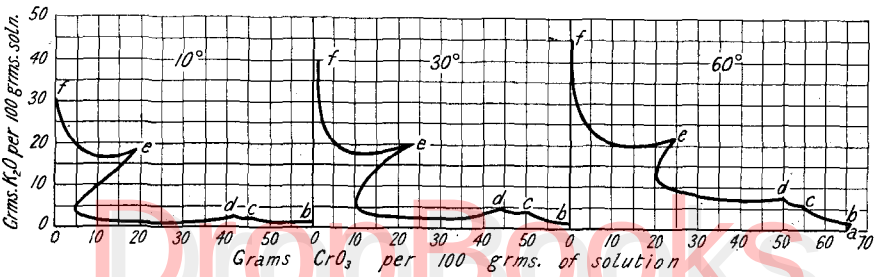



FIG. 36.—Equilibrium Diagram for the Ternary System: $K_2O$–$CrO_3$–$H_2O$ at 30°.




FIGS. 37, 38, and 39.—Solubility of Potassium Chromate in Solutions of Chromic Acid.

and F. Hiebenthal found the solubility of potassium chromate, *S*, in the presence of *n*-normal soln. of various salts:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| NaCl | *n* | 0 | 0·42 | 0·86 | 1·73 | 2·59 | 3·30 | 3·40 | 4·25 |
| | *S* | 8·35 | 8·11 | 7·71 | 6·51 | 5·46 | 4·79 | 4·57 | 4·49 |
| KCl | *n* | 0·40 | 0·46 | 1·31 | 1·72 | 2·18 | 2·70 | — | — |
| | *S* | 7·76 | 7·69 | 6·48 | 5·89 | 5·24 | 4·75 | — | — |
| KBr | *n* | 0·41 | 0·82 | 1·24 | 1·78 | 2·19 | 2·70 | — | — |
| | *S* | 7·56 | 6·91 | 6·26 | 5·50 | 5·00 | 4·38 | — | — |
| $MgCl_2$ | *n* | 0·42 | 0·86 | 1·73 | 2·27 | 2·76 | 3·26 | — | — |
| | *S* | 7·58 | 6·11 | 4·30 | 2·74 | 1·30 | 1·04 | — | — |
| $NH_4Cl$ | *n* | 0·45 | 0·83 | 1·81 | 2·34 | 2·73 | 3·76 | 4·51 | — |
| | *S* | 7·68 | 6·92 | 5·58 | 5·00 | 4·43 | 3·49 | 2·87 | — |

for NaCl, $S=8·770-1·24n$; for KCl, $S=8·287-1·31n$; for KBr, $S=8·129-1·39n$; for $MgCl_2$, $S=8·697-2·68n$; and $NH_4Cl$, $S=8·318-1·425n$.

The rhombic, bipyramidal crystals are pseudohexagonal, and, according to E. Mitscherlich, have the axial ratios $a:b:c=0·5694:1:0·7298$. W. Brendler gave $a:b:c=0·5694:1:0·7298$ for crystals of tarapacaite. Observations on the crystals of potassium chromate were also made by H. J. Brooke, H. Baumhauer, H. Topsöe and C. Christiansen, F. Corio, W. J. Grailich and V. von Lang, F. Corio, A. Hettich and A. Schleede, etc. The habit was found by H. de Sénarmont to be tabular when the crystals are grown in a soln. of sodium carbonate; but J. W. Retgers said that the crystals are those of $K_3Na(CrO_4)_2$, and not of potassium chromate. R. Marc and W. Wenk found that the velocity of crystallization of fused potassium chromate is three-fourths the speed of that of fused potassium sulphate; O. Schott, that a soln. of the salt in molten potassium nitrate furnishes

crystals with a habit different from that which later obtains; while O. Lehmann said that the habit of the crystals under these conditions is unchanged. The (010)- and (001)-cleavages are clear. O. Lehmann observed the development of cleavage planes as the solid is heated. K. Herrmann and co-workers found the X-radiograms of the rhombic bipyramidal crystals of potassium chromate have a simple lattice with four mols. per unit cell, with $a$=7·45 A., $b$=10·3 A.; and $c$=5·88 A. E. Kochholm and N. Schönfeldt studied the isomorphism of this salt with potassium sulphate and selenate. H. Topsöe and C. Christiansen found that the optical character is negative, and the optic axial angle $2V$=51° 40′; and $2E$=97° 30′. W. J. Grailich and V. von Lang gave $2E$=92°. A. des Cloizeaux gave $2E$=100° 32′ for red-light, 95° 40′ for blue-light, and 93° 10′ for blue-light. H. de Sénarmont, and W. J. Grailich and V. von Lang found that the optic axial angles increase with a rise of temp. L. Stibing gave for the axial ratios of solid soln. of potassium sulphate and chromate with 0·5 molar per cent. of potassium chromate $a:b:c$=0·5727 : 1 : 0·7434; 0·19 per cent., 0·5723 : 1 : 0·7436; 2·44 per cent., 0·5719 : 1 : 0·7445; 8·26 per cent., 0·5715 : 1 : 0·7444; 38·47 per cent.,

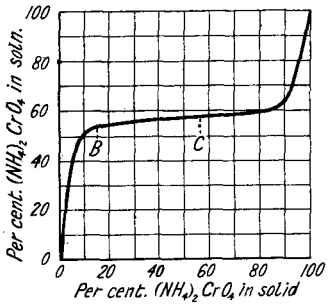



FIG. 40.—Solubility of the Binary System: $(NH_4)_2CrO_4$–$K_2CrO_4$ at 25°.

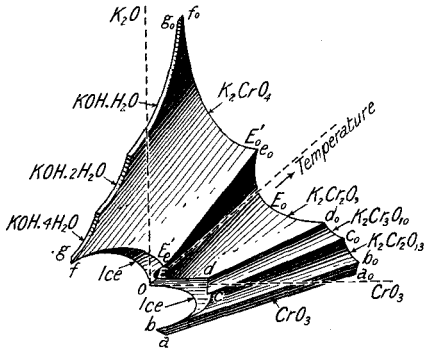



FIG. 41. — Equilibrium Model for the System: $K_2O$–$CrO_3$–$H_2O$ at different Temperatures.

0·5712 : 1 : 0·7418; 90·59 per cent., 0·5704 : 1 : 0·7381; and 100 per cent. 0·5696 : 1 : 0·7351 when potassium sulphate alone has 0·5727 : 1 : 0·7418. The topic axes of potassium chromate are $\chi:\psi:\omega$ =3·9708 : 4·0113 : 5·1244, when those of potassium sulphate are 3·8576 : 3·8805 : 4·9968. E. Pietsch and co-workers studied the attack of the edges and corners of the crystals by sulphuric acid.

T. Ishikawa studied the system: $(NH_4)_2SO_4$–$(NH_4)_2CrO_4$–$K_2CrO_4$–$K_2SO_4$; and S. Araki found the solubility curves for the system $(NH_4)_2CrO_4$–$K_2CrO_4$–$H_2O$ at 25°. The curve has two branches with two series of solid soln., and a gap with between 16·75 and 55·50 molar per cent. of ammonium chromate, *BC*, Fig. 40. According to S. F. Schemtschuschny, the cooling curve of potassium chromate exhibits two transition points, one at 984° corresponding with the crystallization of the molten liquid, and another at 679° corresponding with the conversion of the solid into another crystalline form, Fig. 42. This transition is attended by a change of the yellow into a red salt on heating. E. Groschuff said that this change of colour is evident at 260°, and that the change is gradual so that

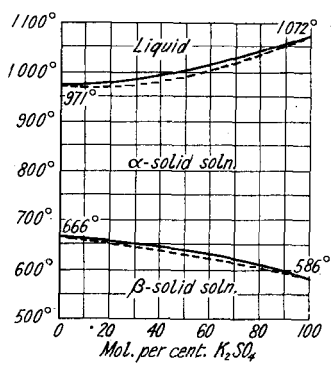



FIG. 42.—The Effect of Potassium Sulphate on the Freezing and Transition Points of Potassium Chromate.

it does not appear to be connected with the transition point. F. Rinne observed the reversibility of the colour changes when the salt is heated by the bunsen flame. E. Groschuff placed the transition temp. at 666° ; and A. Hare, at 660°. The $\alpha$-form is stable above 666°, and is completely miscible with the hexagonal form of potassium sulphate so that the high temp. form is itself hexagonal ; as the ordinary or $\beta$-form of potassium chromate is completely miscible with the $\beta$-form of potassium sulphate. Neither the f.p. curve, nor the transition curves, Fig. 42, shows a maximum or minimum. M. Amadori obtained a similar equilibrium diagram. Yellow potassium chromate, stable at ordinary temp., is isomorphous with potassium sulphate, and, therefore, cannot be separated from that salt by fractional crystallization. W. von Behren and J. Traube studied the dissolution and crystallization of the salt. R. Kollmann, G. Tammann and A. Sworykin, E. Mitscherlich, P. Groth, C. F. Rammelsberg, and J. W. Retgers said the salt is isomorphous with potassium sulphate, selenate, and permanganate. G. Tammann discussed the protection of one salt by another in the case of solid soln. of potassium chromate and sulphate in a soln. of the sulphate. H. Rose observed that a mixture of eq. proportions of sodium sulphate and potassium chromate yields a brittle mass which dissolves in water and yields crystals resembling potassium sulphate. The optical properties of solid soln. of potassium sulphate and chromate were examined by L. Stibing, G. N. Wyrouboff, and E. Mallard ; and the solubility and sp. gr. of soln. of the two salts were examined by M. Herz, A. Fock, and M. Amadori. G. Meyer studied the application of the partition law to the solid soln. of potassium sulphate and chromate in aq. soln. M. Amadori gave for the solubility of potassium chromate in the presence of the sulphate :

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $K_2SO_4$ . | 69·88 | 58·78 | 40·86 | 27·65 | 13·53 | 7·51 | 4·35 | 0 |
| $K_2CrO_4$ . | 0·00 | 22·44 | 75·34 | 140·7 | 266·5 | 315·7 | 324·5 | 332·3 |

so that the curve is in agreement with the results obtained by A. Fock, but not with those of M. Herz. The mutual solubility of the two salts in the solid state is complete ; and the more soluble salt is always in greater proportion in the soln. than in the crystals. The solubility curve of potassium chromate and molybdate is similar. L. Stibing gave for mixtures of potassium sulphate and chromate in soln. and solid soln., when the composition is expressed in molar per cent. $K_2CrO_4$ per litre :

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Soln. . | 0·0741 | 0·2642 | 0·6281 | 0·7543 | 1·0197 | 1·8450 | 2·6867 |
| Solid . | 0·0053 | 0·02337 | 0·0294 | 0·0355 | 0·1603 | 0·1892 | 0·5795 |

A. Fock's results at 25° are summarized in Fig. 42. T. V. Barker studied parallel overgrowths on alkali sulphates and chromates. H. E. Buckley studied the effect of chromates on the crystallization of sodium chlorate.

T. Thomson gave 2·612 for the sp. gr. of potassium chromate ; C. J. B. Karsten, 2·6402 ; H. Kopp, 2·705 ; L. Playfair and J. P. Joule, 2·711 to 2·72309 at 4° ; S. Holker, 2·678 at 15·5° ; H. Schiff, 2·691 ; F. Stolba, 2·7343 ; H. G. F. Schröder, 2·719 to 2·722 ; J. W. Retgers, 2·727 ; A. Cavazzi, 2·691 at 15° ; B. Gossner, 2·741 ; J. L. Andreae, 2·7319 at 18° ; and W. Spring,

| | 0° | 10° | 20° | 40° | 60° | 80° | 100° |
|---|---|---|---|---|---|---|---|
| Sp. gr. . | 2·740 | 2·737 | 2·735 | 2·729 | 2·723 | 2·711 | 2·7095 |

W. Spring, and L. Stibing observed the sp. gr. of solid soln. of potassium chromate and sulphate, and the values calculated by the additive rule :

| | | | | | | |
|---|---|---|---|---|---|---|
| $K_2CrO_4$ . | 0·5080 | 1·2065 | 2·7093 | 9·3837 | 40·5333 | 91·5450 per cent. |
| Sp. gr. (Cals.) | 2·6664 | 2·6669 | 2·6680 | 2·6732 | 2·6959 | 2·7345 ,, |
| Sp. gr. (Obs.) | 2·666 | 2·667 | 2·668 | 2·673 | 2·696 | 2·735 ,, |

F. Fouqué found that the sp. gr. of aq. soln. of potassium chromate with 0·97, 3·35, and 20·57 grms. of salt per 100 grms. of water are respectively 1·0077, 1·0268, and 1·1533 at 0°/4° ; 1·0065, 1·0257, and 1·1500 at 16·4°/4° ; 0·9836, 1·0013, and

DropBooks

1·1165 at 75·5°/4°; and 0·9679, 0·9861, and 1·1065 at 99°. Observations were also made by P. Kremers, R. L. Datta and N. R. Dhar, P. F. Gaehr, and A. Heydweiller. For soln. of the following percentage composition, at 195°, H. Schiff, and G. T. Gerlach found:

| $K_2CrO_4$ . | 1 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 per cent. |
|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. . | 1·0080 | 1·0492 | 1·0837 | 1·1287 | 1·1765 | 1·2274 | 1·2808 | 1·3386 | 1·3991 |

H. Schiff represented his results for soln. with $p$ per cent. of $K_2CrO_4$ by $S=1+0{\cdot}008p+0{\cdot}0_43324p^2+0{\cdot}0_64048p^3$ at 19·5°. F. Flöttmann found the sp. gr. of soln. sat. at 15°, 20°, and 25° to be, respectively, 1·3749, 1·3785, and 1·3805. A. Cavazzi measured the expansion in vol. which occurs when potassium chromate is dissolved in water. K. F. Slotte found the sp. gr. of a soln. with 24·26 per cent. $K_2CrO_4$ at 18° to be 1·2335; and the viscosity (water 100), 133·3 at 10°; 106·5 at 20°; 87·9 at 30°; and 74·3 at 40°. The drop weight of the salt just above its m.p. was found by I. Traube to be 238 mgrms. (water 100). J. Wagner found for $N$-, 0·5$N$-, 0·25$N$-, and 0·125$N$-soln. the viscosity (water unity) 1·1133, 1·0528, 1·0224, and 1·0116 respectively. L. J. Simon mixed equimolar soln. of chromic acid and potassium or sodium hydroxide, and found that discontinuities occur in the viscosity curves when the composition of the soln. corresponds with either the normal chromates or the dichromates, the precise form of the curves depending on whether the relative proportion of the two soln. is taken as the abscissa or the viscosities for soln. of equimolar conc. are compared. Except in high concentrations, the viscosities of eq. soln. of sodium chromate and sodium sulphate, and of potassium chromate and potassium sulphate are identical, and it is concluded that within certain conc. limits, isomorphous solutes produce the same change in the viscosity of the aq. solvent. T. Graham made some observations on the diffusion of potassium chromate into a soln. of potassium acetate; and J. C. G. de Marignac, on the diffusion in the presence of potassium carbonate, or nitrate. Experiments on the diffusion of soln. of chromic acid were also made by F. Rudorff, and H. de Vries. G. Jander and A. Winkel gave 0·77 for the diffusion coeff. of the anion. W. Spring found that with the vol. of potassium chromate unity at 0°, the vol., $v$, at different temp. is:

| | 10° | 20° | 30° | 40° | 60° | 80° | 100° |
|---|---|---|---|---|---|---|---|
| $v$ . | 1·001064 | 1·002114 | 1·003140 | 1·004228 | 1·006439 | 1·009023 | 1·011344 |

which makes the coeff. of cubical expansion 0·00011344 between 0° and 100°, a result very close to that obtained by L. Playfair and J. P. Joule; J. L. Andreae gave 0·000101 between 18° and 56°. W. Spring also found that the coeff. of cubical expansion is very close to that of ammonium and rubidium sulphates. H. Kopp observed the sp. ht. of the crystalline salt to be 0·189 between 18° and 47°; H. V. Regnault gave 0·1850 between 17° and 98°; and F. E. Neumann, 0·1840. J. C. G. de Marignac gave for the sp. ht. of soln. of a mol of potassium chromate in 50, 100, and 200 mols of water between 20° and 51°, respectively 0·8105, 0·8896, and 0·9407; while H. Faasch gave for 0·499$N$-, 0·990$N$-, 1·994$N$-, and 3·986$N$-$K_2CrO_4$, respectively 0·939, 0·898, 0·810, and 0·703 at 18°. The subject was discussed by N. de Kolossowsky. J. J. Berzelius observed that the lemon-yellow salt becomes bright red when heated, but undergoes no further change; it is liable to decrepitate violently before fusion at a red-heat, and emits a green light during fusion; and the molten salt, said G. Magnus, crystallizes as it cools. H. le Chatelier first gave 975° for the m.p., and later,

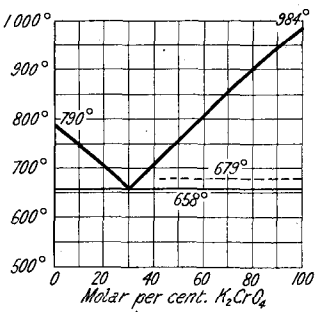



FIG. 43.—Freezing-point Curve of the Mixtures of $K_2CrO_4$–$K_2SO_4$.

940°; S. F. Schemtschuschny, 984°; E. Groschoff, 971°; and M. Amadori, 978°. D. F. Smith and F. A. Hartgen studied this subject. For the transition temp., *vide supra*. H. le Chatelier, E. Groschuff, and M. Amadori studied the m.p. of mixtures of potassium sulphate and chromate—*vide* Fig. 43—a continuous series of solid soln. is formed. M. Amadori obtained continuous series of solid soln. with potassium chromate and potassium molybdate or tungstate. S. F. Schemtschuschny studied the m.p. of the binary system $K_2CrO_4$–KCl, and found a typical V-curve with a eutectic at 658°, and 31·5 molar per cent. of $K_2CrO_4$; no solid soln. are formed on the potassium chloride branch of the curve, but the other branch shows that solid soln. are formed with mixtures containing about 4 molar per cent. of potassium chloride, Fig. 43. F. Guthrie found that a mixture of potassium chromate and nitrate has a eutectic at 295° and 96·2 per cent. of the nitrate; for mixtures of potassium chromate and dichromate, *vide infra*. The lowering of the f.p. of soln. of $w$ grms. of $K_2CrO_4$ in 100 grms. of water, was measured by L. C. de Coppet, and F. Rüdorff; while I. Koppel and E. Blumenthal gave:

| $K_2CrO_4$ | 4·53 | 6·12 | 26·99 | 31·33 | 42·04 | 54·57 |
|---|---|---|---|---|---|---|
| Lowering f.p. | 0·99° | 1·2° | 4·3° | 5·7° | 7·12° | 11·37° |

For the eutectic temp., *vide supra*. G. Tammann gave for the lowering of the vap. press. for soln. with $w$ grms. of $K_2CrO_4$ per 100 grms. of water,

| $K_2CrO_4$ | 10·93 | 14·29 | 26·63 | 34·89 | 46·99 | 53·28 |
|---|---|---|---|---|---|---|
| Lowering v.p. | 18·0 | 22·7 | 40·4 | 52·1 | 73·7 | 84·1 mm. |

I. Bencowitz and H. T. Hotchkiss, and F. M. Raoult made some observations on this subject. According to M. Alluard, the b.p. of a sat. soln. of the chromate is 104·2° at 718 mm.; according to P. Kremers, 107°; and according to I. Koppel and E. Blumenthal, 105·8° at 760 mm. A. Hare found the heat of the polymorphic transformation of potassium chromate at 660° to be 2·45 Cals. per mol. R. Lorenz and W. Herz studied some relations between the b.p. and critical temp. The heats of neutralization given by M. Berthelot are $(CrO_{3aq.},2KOH_{aq.})$=30·4 Cals. at 12°; with the solid compounds, 95·6 Cals.; with $K_2Cr_2O_7$ (in 12 litres) and 2KOH (in 4 litres), M. Berthelot gave 23·6 Cals., and P. Sabatier, 23·0 Cals.; and for $H_2CrO_4$ (in 8 litres) and 2KOH (in 4 litres). M. Berthelot gave 27·738 Cals., and P. Sabatier, 25·4 Cals. M. Berthelot also gave for $(2Cr(OH)_{3precipitated},4KOH_{aq.},3O)$=61·4 Cals. at 8°; and for solid hydroxide and chromate, 101·9 Cals. F. Morges gave −5·254 Cals. for the heat of soln. in 543 mols of water at 19·5°.

H. Topsöe and C. Christiansen gave for the index of refraction, 1·7131 for the *C*-line; 1·7154 for the *D*-line; and 1·7703 for the *F*-line. E. Mallard gave for red-light, $\alpha$=1·6873, $\beta$=1·722, and $\gamma$=1·7305. F. Fouqué, and R. L. Datta and N. R. Dhar measured the refractive indices of aq. soln.; and A. Heydweiller gave for the *D*-line at 18°:

| $K_2CrO_4$ | 0·1*N*- | 0·2*N*- | 0·5*N*- | 1·0*N*- | 2·0*N*- | 4·0*N*- |
|---|---|---|---|---|---|---|
| $\mu$ | 1·33529 | 1·33732 | 1·34335 | 1·35305 | 1·37188 | 1·40709 |

F. Flöttmann found the index of refraction of soln. sat. at 15°, 20°, and 25° to be respectively 1·43267, 1·43276, and 1·43288. H. Fromherz studied the absorption spectrum. L. R. Ingersoll found Verdet's constant for the electromagnetic rotatory power for light of wave-length 0·6, 0·8, 1·0, and 1·25$\mu$ to be respectively 0·0092, 0·0060, 0·0041, and 0·0026 for soln. of sp. gr. 1·372. T. Thomson said that one part of the salt imparts a distinct yellow colour to 40,000 parts of water. The spectroscopic observations of H. Becquerel, W. Böhlendorff, A. Étard, F. Grunbaum, J. M. Hiebendaal, J. H. Jones and W. W. Strong, E. Viterbi and G. Krausz, O. Knoblauch, P. Sabatier, J. L. Soret, H. Settegast, A. M. Taylor, T. Aden, N. R. Tawde and E. R. Paranjpe, E. Jander, and K. Vierordt have been pre-

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viously discussed. C. Schaefer and M. Schubert found in the ultra-red spectrum a well-defined maximum at 11·16$\mu$ with soln. of potassium chromate, and at 11·2$\mu$ with soln. of potassium sodium chromate. H. von Halban and K. Siedentopf studied the absorption of light in cells of potassium chromate and hydroxide soln., and soln. of potassium chromate and copper sulphate in aq. ammonia. A. E. Lindh, D. Coster, and O. Stelling studied the X-ray spectrum ; and D. M. Yost, the absorption of X-rays. I. Plotnikoff and M. Karshulin measured the absorption spectrum and the region of photochemical sensitivity for soln. of potassium chromate in colloidion films—with methyl alcohol as acceptor. A. Kailan found that an aq. soln. of potassium chromate is reduced by radium rays more slowly than potassium dichromate. E. Montignie observed that after exposure to ultra-violet light, potassium chromate affects a photographic plate.

J. A. Fleming and J. Dewar found that the dielectric constant of water is raised a little by potassium chromate, and at —88·5°, the dielectric constant of the frozen mixture is between 3 and 10—when with ice alone, the constant is 2·5. W. Schneider studied the piezoelectric effect; P. Walden, and A. Heydweiller, the electrical conductivity of aq. soln. P. Walden gave for the eq. conductivity, $\lambda$ mhos, at 8°. with a gram-equivalent of the salt in $v$ litres,

| $v$ | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|
| $\lambda$ | 129·6 | 136·3 | 141·3 | 145·5 | 148·3 | 150·4 |

H. C. Jones and C. A. Jacobson measured the molar conductivity, $\mu$ mhos, between 0° and 35°, and A. M. Clover and H. C. Jones, between 35° and 65°, for a mol of the salt in $v$ litres ; and calculated values for the percentage ionization, $\alpha$ ;

| $v$ | | 2 | 8 | 16 | 32 | 128 | 512 | 1024 | 2048 |
|---|---|---|---|---|---|---|---|---|---|
| $\mu$ | 0° | 102·9 | 118·6 | 125·6 | 132·8 | 149·3 | 156·8 | 160 | 161·4 |
| | 125° | 136·6 | 161·9 | 174·3 | 185·2 | 204 | 219 | 223 | 225 |
| | 25° | 176·6 | 209 | 228 | 242 | 270 | 290 | 294 | 298 |
| | 35° | 211 | 251 | 273 | 290 | 323 | 349 | 352 | 356 |
| | 50° | 266 | 317 | — | 366 | 415 | 442 | — | — |
| | 65° | 316 | 381 | — | 445 | 429 | 548 | — | — |
| $\alpha$ | 0° | 63·7 | 73·5 | 77·8 | 82·5 | 92·5 | 97·2 | 99·1 | 100·0 |
| | 35° | 59·6 | 70·4 | 76·6 | 81·4 | 90·6 | 98·1 | 98·8 | 100·0 |

Conductivity observations were also made by R. Lenz, and E. Bouty. N. R. Dhar said that electrical conductivity and coagulation experiments agree that in soln. the dichromate is in part present as $KHCrO_4$. F. Morges observed that in the electrolysis of an aq. soln. of the chromate, potassium hydroxide accumulates about the cathode, and the oxygen given off at the anode forms dichromate—*vide supra.* chromic acid. As indicated in connection with chromic acid, calculations on the degree of ionization are unsatisfactory on account of the conversion of chromates to dichromates in aq. soln. J. Lundberg's observations on the hydrolysis of these soln. were indicated in connection with chromic acid. The aq. soln. has an alkaline reaction towards lacmoid, litmus, and phenolphthalein, and observations on this subject were made by M. M. Richter, R. T. Thomson, and J. A. Wilson. H. M. Vernon estimated the degree of ionization from the colour. G. Baborovsky studied the electrolytic reduction of the salt ; and P. Düllberg, the electrometric titration with hydrochloric acid. L. A. Welo gave $0{\cdot}04\times10^{-6}$ for the magnetic susceptibility. G. Gore electrolyzed fused potassium chromate and obtained a deposit on the cathode.

J. Obermiller measured the hygroscoposity of the crystals. H. Moser said that potassium chromate is not decomposed when heated to redness—*vide supra,* chromium trioxide. W. Ipatieff and co-workers found that hydrogen under a press. of 200 atm. reduces soln. of potassium chromate ; and with a soln. of potassium chromate and sulphuric acid, $Cr_2(SO_4)_3.Cr_2O_3.K_2O.H_2O$ is formed. G. Gore observed that the salt becomes red in compressed hydrogen chloride, but in liquid hydrogen chloride it is neither changed nor dissolved. A. C. Robertson studied the action of potassium chromate on hydrogen dioxide : $2K_2CrO_4+H_2O_2=K_2Cr_2O_7$

$+2KOH+O$—*vide supra*, potassium dichromate; and *vide supra*, chromic acid. G. Grasser and T. Nagahama found that the reduction with many reducing agents is incomplete unless an acid be present. J. W. Thomas found that the salt is decomposed by dry hydrogen chloride forming potassium chloride and dichromate; the dichromate is then converted into chromium trioxide, and this is then reduced to a brown chromic oxide without forming chromyl chloride. M. Bobtelsky studied the oxidation of conc. hydrochloric acid by potassium chromate. W. B. Morehouse found the X-ray absorption of the system: $K_2Cr_2O_7+16KI+14HCl \rightarrow 8KCl+2CrCl_3+4I_2+8KI+7H_2O$ is 0·25 per cent. greater after the reaction than it is before. E. Ramann and H. Sallinger measured the precipitation ratio, *i.e.* the ratio in which silver divides itself between the iodate and chromate in the reaction: $K_2CrO_4+2AgIO_3=2KIO_3+Ag_2CrO_4$. J. L. Lasssaigne found that when heated with sulphur, chromic oxide and potassium sulphate and sulphide are formed: $8K_2CrO_4+(3n+5)S=5K_2SO_4+3K_2S_n+4Cr_2O_3$; initially, said O. Döpping, some thiosulphate is produced. K. Brückner said that when the mixture of chromate and sulphur is heated for a short time, potassium sulphide and thiosulphate are formed, and afterwards potassium sulphate and polysulphide as well as chromic sulphide and oxide. As the heating continues, the sulphide is slowly oxidized, and the end-products are potassium sulphate, and chromic oxide with traces of chromates, and chromium sulphide. J. B. Senderens represented the reaction when the aq. soln. is boiled with sulphur, by $6K_2CrO_4+15S+9H_2O=6Cr(OH)_3+5K_2S_2O_3+K_2S_5$; and O. Döpping, the reaction with potassium pentasulphide, by $8K_2CrO_4+2K_2S_5+5H_2O=5K_2S_2O_3+10KOH+4Cr_2O_3$. The reaction between the heated salt and dry hydrogen sulphide was found by W. Müller to furnish water, potassium and chromium sulphides and chromic oxide; with an aq. soln. of the chromate, saturated with sodium hydroxide, T. L. Phipson found that green chromic hydroxide is precipitated—*vide infra*, chromium sulphide. W. R. Hodgkinson and J. Young studied the action of dry sulphur dioxide on the salt. W. Müller represented the reaction between the heated salt and the vapour of carbon disulphide by $2K_2CrO_4+5CS_2=2K_2S_3+Cr_2S_3+4CO+CO_2+SO_2$. P. Berthier said that sulphur dioxide precipitates brown chromic chromate from an aq. soln. of potassium chromate. The precipitate then dissolves forming a green liquid containing potassium hydroxide, chromic oxide and sulphuric, sulphurous, and dithionic acids. P. Job found that 0·01 to 0·001*M*-$K_2CrO_4$, reacts with sulphuric acid, so that the reaction $CrO_4'' + H^{\cdot} \rightleftharpoons HCrO_4'$ has an ionization constant $K=7\times10^{-5}$ at 15°. E. Pietsch and co-workers studied the surface conditions in the reaction between potassium chromate and sulphuric acid. E. C. Franklin and C. A. Kraus found the chromate to be insoluble in liquid ammonia. H. Stamm found that soln. with 0, 1·350, and 3·517 grms. of $NH_3$ per 100 grms. of water dissolve 0·3218, 0·0324, and 0·0036 mol of $K_2CrO_4$ respectively. R. C. Woodcock, and F. Mohr found that when the chromate is distilled with ammonium chloride and water, ammonia and potassium dichromate are formed. F. Santi found that ammonium chloride converts chromates to dichromates and dichromates to chromic acid; and E. Divers that chromates react with a soln. of ammonium nitrate in aq. ammonia. H. P. Cady and R. Taft observed that potassium chromate is appreciably soluble in phosphoryl chloride. J. T. Cooper observed that a yellow soln. of chromate gradually turns green in the presence of arsenic trioxide. H. Moser observed the decomposition of potassium chromate mixed with carbon and heated—potassium carbonate and chromic oxide are formed. E. Fleischer observed that the aq. soln. of the chromate attracts carbon dioxide from the atm. When the chromate is heated in a current of carbon monoxide, F. Göbel observed that chromic oxide is formed; and K. Stammer added that potassium carbonate, carbon dioxide, and potassium chromite are also produced. J. Jacobson found that when carbon, gun cotton, and other organic substances are soaked in a soln. of potassium chromate and dried, they burn more vigorously than before. F. W. O. de Coninck observed that 100 grms. of a soln. of glycol sat. at 15·4, contain 1·7 grms. of potassium

chromate. A. Naumann found the chromate to be insoluble in benzonitrile, and in methyl acetate; and A. Naumann, and W. Eidmann, insoluble in acetone. It is also insoluble in alcohol. F. Göbel found that potassium chromate is partially decomposed when heated in carbon monoxide, and chromic oxide is formed. G. Stadnikoff studied the adsorption of potassium chromate by aniline-black. S. Glasstone and co-workers studied the effect of the chromate on the solubility of ethyl alcohol. F. Tassaert observed that when the chromate is heated with acetic acid and alcohol, it is partly transformed into potassium and chromic acetates. According to F. Tassaert, many acids—sulphuric, hydrochloric, nitric, and acetic acids—abstract half the alkali, and form potassium dichromate, which, if the soln. be sufficiently concentrated, is precipitated—*vide supra*, chromium trioxide. E. Schweizer said that carbonic acid acts similarly, and F. Margueritte, boric acid; but F. Mohr added that boric and silicic acids, and potassium hydrocarbonate do not act in this way, but that formic, acetic, butyric, and valerianic acids do transform chromate into dichromate. If soln. of the potassium salts of one of these four acids be evaporated with potassium dichromate, potassium chromate is formed. F. Mohr added that potassium hydrocarbonate acts similarly. According to E. Schweizer, a soln. of potassium dichromate with sodium stearate precipitates stearic acid; benzoic acid forms potassium benzoate and dichromate when treated with potassium chromate, and when the soln. is evaporated, potassium chromate and benzoic acid are reformed. A soln. of sodium benzoate and potassium dichromate does not yield chromate on evaporation. Salicylic acid behaves like benzoic acid. Normal potassium urate reacts with the chromate forming uric acid and potassium dichromate. M. Berthelot, and P. Sabatier studied the reaction of the chromate with acids. According to J. W. Döbereiner, a soln. of barium hydroxide gives a quantitative precipitate of barium chromate. According to L. Meyer, an aq. soln. of potassium chromate in contact with crystals of copper sulphate, silver nitrate, mercurous nitrate, or mercuric chloride forms potassium dichromate and a little basic chromate is precipitated; lead acetate is not changed; cobaltous chloride gives a precipitate—*vide supra*, reactions of chromates. K. W. Floroff studied the reaction $BaSO_4+K_2CrO_4=K_2SO_4+BaCrO_4$. L. Kahlenberg and W. J. Trautmann observed no reaction when the chromate mixed with silicon is heated in a hard glass tube by a bunsen burner, but there is a strong reaction when heated by a méker burner. A. C. Robertson represented the reaction with vanadic acid: $2K_2CrO_4+H_2O_2+HVO_3=K_2Cr_2O_7+2KOH+HVO_4$. R. F. Reed and S. C. Horning showed that potassium chromate in aq. soln. is absorbed by zinc, possibly as potassium or zinc chromate.

S. W. Johnson cooled by a freezing mixture a hot soln. of potassium dichromate in conc. ammonia, and obtained crystals of **ammonium potassium chromate,** $(NH_4)KCrO_4$; E. Kopp obtained the same salt by evaporating the soln. over caustic alkali. The rhombic, pale sulphur-yellow prisms are isomorphous with potassium sulphate. E. Maumené said that the salt turns brown at 240° owing to the formation of the chromate of a base $N_2H_6O$, and that the salt is completely decomposed at 270° leaving residual chromic oxide. P. Sabatier gave 10·6 Cals. for the heat of formation from a soln. of potassium dichromate; or 15·5 Cals. from the solid salts; the heat of soln. for 173·4 grms. of salt in 40 times its weight of water at 17° is —5·3 Cals. S. W. Johnson found that the salt loses ammonia when exposed to air, and when the soln. is boiled or evaporated there remains potassium dichromate. E. Kopp said that sodium thiosulphate has no action in the cold, but when heated, chromic chromate is formed. A. Étard's analysis indicates that the salt is monohydrated; but S. W. Johnson's analysis shows that the salt is anhydrous. J. Zehenter prepared $2(NH_4)_2CrO_4.3K_2CrO_4$, by adding an. eq. of potassium carbonate to a conc. soln. of ammonium dichromate, and precipitating with alcohol. The sulphur-yellow needles have a sp. gr. 2·403 at 15°. They are stable when dry. H. Traube prepared **lithium potassium chromate,** $LiKCrO_4$, in hexagonal or pseudo-hexagonal crystals isomorphous with the analogous sul-

phate; J. Zehenter gave 2·539 for the sp. gr. at 15°. H. Rose melted 2 parts of potassium dichromate and one of sodium carbonate; the cold mass dissolved in hot water deposits, on cooling, crystals of **potassium sodium chromate,** or *chromoglaserite*, or *chromatoglaserite*, $3K_2CrO_4.Na_2CrO_4$, or $K_3Na(CrO_4)_2$—the crystallization is attended by crystalloluminesce. J. Zehenter obtained the salt by evaporating a hot soln. of potassium dichromate neutralized with sodium carbonate; and C. von Hauer, by evaporating a mixed soln. of 3 mols of potassium chromate and one mol of sodium chromate. The yellow crystals were found by B. Gossner to be trigonal with the axial ratio $a:c=1:1{\cdot}2857$ and $\alpha=88°\ 28'$, there is a second variety in monoclinic crystals with $a:b:c=0{\cdot}5833:1:0{\cdot}8923$, and $\beta=90°\ 46'$. H. Steinmetz said that there is a gradual change in the chromate, $K_3Na(CrO_4)_2$, between 150° and 175° without appreciable change of vol. or coeff. of expansion. The sp. gr. is 2·719 at 15°; at 14°, 100 parts of water dissolve 64·2 parts of salt. According to J. Zehenter, the mother-liquor yields a hemihydrate, of sp. gr. 2·575 at 15°. It loses water at 150°; and 100 parts of water at 14° dissolve 66·4 parts of salt. E. Flach measured the f.p. of mixtures of sodium and potassium chromates, and the results are summarized in the upper curve of Fig. 44. The solid soln. of the two salts shows breaks in the cooling curve corresponding with the lower curve of Fig. 44. There are thus indications of the formation of the trigonal chromatoglaserite analogous to ordinary or sulphatoglaserite, $3K_2SO_4.Na_2SO_4$. This complex salt can form solid soln. to a limited extent with sodium chromate, so that during the cooling the hexagonal crystals of the solid soln. between 669° and 371° mostly split into simple chromates and solid soln. of chromatoglaserite and sodium chromate. The curve of mixtures of potassium and sodium chromates, previously fused together, shows a break corresponding with $K_3Na(CrO_4)_2$. Thus,

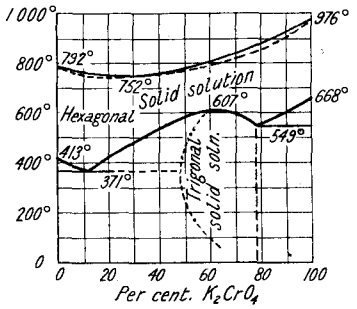


FIG. 44.—Equilibrium Diagram of the Binary System: $Na_2CrO_4$–$K_2CrO_4$.

| $K_2CrO_4$ . | 0 | 10 | 50 | 70 | 78·3 | 90 | 100 per cent. |
|---|---|---|---|---|---|---|---|
| Sp. gr. . | 2·765 | 2·766 | 2·767 | 2·767 | 2·768 | 2·751 | 2·740 |

The crystallographic data are summarized in Table III. The thermal diagram

TABLE III.—CRYSTALLOGRAPHIC DATA OF POTASSIUM AND SODIUM SULPHATES AND CHROMATES.

| | Mol. wt. | Sp. gr. | Mol. vol. | Axial ratios $a:b:c$ | Topic parameters $\chi:\Psi:\omega$ |
|---|---|---|---|---|---|
| $K_2SO_4$ . | 174·27 | 2·666 | 65·37 | 0·5727 : 1 : 0·7418 | 3·0688 : 5·3586 : 3·9750 |
| $K_3Na(SO_4)_2$ | 166·22 | 2·696 | 61·65 | 0·5773 : 1 : 0·7450 | 3·0215 : 5·2334 : 3·8990 |
| $Na_2SO_4$ . | 142·07 | 2·683 | 52·95 | 0·4731 : 1 : 0·7996 | 2·4564 : 5·1922 : 4·1517 |
| $K_2CrO_4$ . | 194·20 | 2·740 | 70·88 | 0·5694 : 1 : 0·7298 | 3·1578 : 5·5452 : 4·0473 |
| $K_3Na(CrO_4)_2$ | 186·15 | 2·768 | 67·25 | 0·5773 : 1 : 0·7423 | 3·1141 : 5·3737 : 4·0038 |
| $Na_2CrO_4$ . | 162·00 | 2·765 | 58·59 | 0·4643 : 1 : 0·7991 | 2·5096 : 5·4051 : 4·3193 |

of mixtures of sulphato- and chromato-glaserites is shown in Fig. 45. The quaternary system: $K_2CrO_4$–$Na_2CrO_4$–$Na_2SO_4$–$K_2SO_4$, was studied by E. Flach and also the same system with water at 30°.

L. Grandeau [5] prepared **rubidium chromate,** $Rb_2CrO_4$, by neutralizing a soln. of the dichromate with rubidium carbonate, and by melting chromic oxide with rubidium nitrate, or with rubidium carbonate in air. The spontaneous evaporation of the aq. soln. furnishes first a crop of crystals of the dichromate, and then the

chromate. The aq. soln. has an alkaline reaction. According to J. Piccard, the yellow crystals are rhombic bipyramids with the axial ratios $a : b : c = 0{\cdot}5665 : 1 : 0{\cdot}7490$. The (001)-cleavage is marked. The optic axial angles found by G. N. Wyrouboff were $2H_0 = 73°\ 46'$ for red-light, and $76°\ 5'$ for green-light; and $2H_0 = 146°$ for white light. The topical character is negative. J. W. Retgers, J. Piccard, and L. Grandeau said that the crystals are isomorphous with potassium chromate, sulphate, and selenate. T. V. Barker studied parallel overgrowths on alkali sulphates and chromates. F. A. H. Schreinemakers and H. Filippo found the percentage solubility, $S$, to be:

| | | | | |
|---|---|---|---|---|
| | −7° | 0° | 10·3° | 20° |
| $S$ . | 36·6 | 38·2 | 40·2 | 42·4 |
| | 30° | 40° | 50° | 60·4° |
| $S$ . | 44·1 | 46·1 | 47·4 | 48·9 |

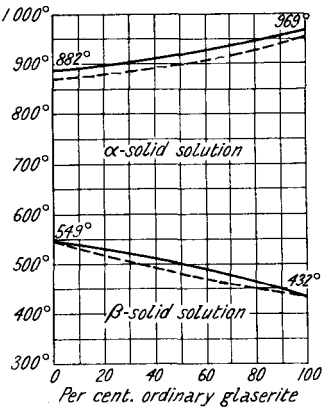


FIG. 45.—The Binary System of Sulphato- and Chromato-glaserites.

They also studied the ternary system: $Rb_2O$–$CrO_3$–$H_2O$ at 30°; and found that with the composition of the soln. expressed in percentages:

| | | | | | | |
|---|---|---|---|---|---|---|
| $CrO_3$ . . | 0 | 0·00 | 11·98 | 15·54 | 4·87 | 15·05 |
| $Rb_2O$ . . | 60·56 | 56·82 | 27·99 | 28·55 | 4·60 | 3·45 |
| Solids | $RbOH.2H_2O$ | | $Rb_2CrO_4$ | | $Rb_2Cr_2O_7$ | |
| $CrO_3$ . . | 15·05 | 24·92 | 14·29 | 58·69 | 63·07 | 62·28 |
| $Rb_2O$ . . | 3·45 | 1·66 | 1·28 | 1·07 | 0·92 | 0 |
| Solids | | $Rb_2Cr_3O_{10}$ | | $Rb_2Cr_4O_{13}$ | | $CrO_3$ |

The results are plotted in Fig. 46; where the solubility curve *ab* refers to the solid phase $CrO_3$; *bc*, to $Rb_2Cr_4O_{13}$; *cd*, to $Rb_2Cr_3O_{10}$; *de*, to $Rb_2Cr_2O_7$; *ef*, to $Rb_2CrO_4$; and *fg*, to $RbOH.nH_2O$.

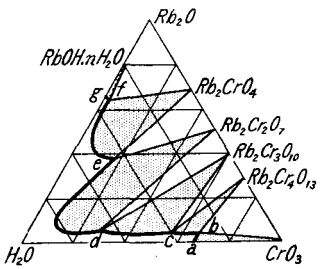


FIG. 46.—Equilibrium Diagram for the Ternary System: $Rb_2O$–$CrO_3$–$H_2O$.

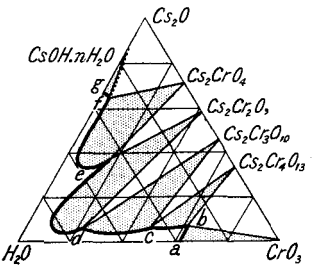


FIG. 47.—Equilibrium Diagram for the Ternary System: $Cs_2O$–$CrO_3$–$H_2O$ at 30°.

C. Chabrié[6] obtained **cæsium chromate,** $Cs_2CrO_4$, by treating silver chromate with a boiling soln. of cæsium chloride, and evaporating the filtrate for crystallization; or more simply from an aq. soln. of chromic acid and cæsium carbonate. According to F. R. Fraprie, the crystals exist in two forms. C. Chabrié's process furnishes the so-called α-crystals in pale yellow, trigonal prisms with the axial ratio $a : c = 1 : 1{\cdot}2314$; while the β-crystals form dark yellow, rhombic bipyramidal crystals with the axial ratios $a : b : c = 0{\cdot}5640 : 1 : 0{\cdot}7577$, and which show twinning about the (130)-plane. These crystals are completely isomorphous with the potassium chromate family—a subject also discussed by J. W. Retgers. T. V. Barker studied

parallel overgrowths on alkali sulphates and chromates. F. A. H. Schreinemakers and D. J. Meijeringh observed that in the ternary system: $Cs_2O$–$CrO_3$–$H_2O$ at 30°, the composition of the soln. expressed in percentages, is:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $CrO_3$ | 0 | 0·119 | 9·662 | 13·08 | 8·98 | 2·16 | 4·57 |
| $Cs_2O$ | 70·63 | 69·22 | 31·68 | 35·08 | 24·05 | 3·04 | 1·61 |
| Solids. | $CsOH.nH_2O$ | | $Cs_2CrO_4$ | | $Cs_2Cr_2O_7$ | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $CrO_3$ | 4·57 | 25·59 | 44·45 | 55·17 | 62·70 | 62·50 | 62·28 |
| $Cs_2O$ | 1·61 | 0·096 | 3·13 | 3·90 | 4·35 | 2·33 | 0 |
| Solids. | | $Cs_2Cr_3O_{10}$ | | $Cs_2Cr_4O_{13}$ | | $CrO_3$ | |

The line *ab*, Fig. 47, is the solubility curve with $CrO_3$ as solid phase; *bc*, with $Cs_2Cr_4O_{13}$; *cd*, with $Cs_2Cr_3O_{10}$; *de*, with $Cs_2Cr_2O_7$; *ef*, with $Cs_2CrO_4$; and *fg*, with $CsOH.nH_2O$. The sodium and ammonium salts are alone hydrated in the ternary systems at 30° and the solubilities of the different alkali chromates at 30° are:

| | Li | Na | $NH_4$ | K | Rb | Cs |
|---|---|---|---|---|---|---|
| $M_2CrO_4$ | 49·98 | 46·63 | 28·80 | 39·63 | 44·14 | 47·0 |

M. Rosenfeld[7] obtained a green precipitate on adding a soln. of cuprous chloride in a conc. soln. of sodium chloride to an excess of a soln. of potassium chromate. The reaction was studied by H. J. P. Venn and V. Edge. Complex precipitates are formed differing in colour and constitution according to the method of preparation. The reaction consists essentially in the oxidation of the cuprous salt, and the formation of basic compounds whose composition changes when they are washed. The ultimate reactions are represented by: $3Cu_2Cl_2+2K_2CrO_4+8H_2O=4KCl+CuCl_2+5Cu(OH)_2+2Cr(OH)_3$, and $3Cu_2Cl_2+K_2Cr_2O_7+7H_2O=2KCl+2CuCl_2+4Cu(OH)_2+2Cr(OH)_3$. Intermediate products are represented by $2CuO.CuCl_2.3H_2O$, and $3CuO.CuCl_2.4H_2O$. J. Schulze reported normal **copper chromate,** $CuCrO_4$, to be formed when copper hydroxide is heated with an excess of a soln. of potassium dichromate in a sealed tube at 220°. Under ordinary conditions, J. Schulze, and M. Prud'homme and F. Binder found that a boiling soln. of the dichromate and copper hydroxide forms a basic chromate. According to G. Brügelmann, and J. C. G. de Marignac, the spontaneous evaporation of an aq. mixture of sat. soln. of copper sulphate and potassium dichromate gives first a crop of crystals of potassium sulphate, and then mixed crystals of chromates of indefinite composition. G. Quincke studied the formation of copper chromate by the diffusion of a soln. of copper sulphate into gelatine containing sodium dichromate. S. H. C. Briggs obtained normal copper chromate from a soln. of 3 grms. of copper carbonate with 6·9 per cent. CuO in 2·4 grms. of chromium trioxide dissolved in 20 c.c. of water, and, when the evolution of carbon dioxide has ceased, heated in a sealed tube for 2 or 3 hrs. at 200°; and also by boiling, in a vessel fitted with a reflux condenser, a mixture of 12 grms. copper carbonate, 21 grms. chromium trioxide, and 15 c.c. of water over an oil-bath; the product was washed with water and dried in a desiccator. H. Kopp, and G. C. Gmelin obtained crystals of copper chromate, isomorphous with pentahydrated copper sulphate, from a soln. of copper hydroxide in aq. chromic acid. M. Prud'homme said that if a soln. of chromic and cupric oxides in alkali-lye be allowed to stand some months, it deposits crystals of cupric chromate. H. W. Morse studied the rhythmic precipitation of the chromate.

J. Schulze said that the crystals are iron-black or reddish-brown with the appearance of hæmatite; the salt forms copper chromite at 400°. L. and P. Wöhler found that decomposition begins at 325°; at 340°, the partial press. of the oxygen is 417 mm.; and at 380°, over 750 mm. No state of equilibrium was observed. At 650°, cuprous chromite is formed. J. Schulze said that cupric chromate is insoluble in water, but it is soluble in acids including chromic acid. The salt is hydrolyzed by boiling water, leaving a basic chromate—possibly $3CuO.CrO_3.2H_2O$—as a residue. S. H. C. Briggs said that cupric chromate is not soluble in a soln. of copper sulphate.

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According to M. C. Schuyten, when an aq. soln. of copper sulphate and potassium dichromate is treated with ammonia, or if potassium dichromate be added to an ammoniacal soln. of cupric hydroxide from which the excess of ammonia has been removed by exposure to air, **copper tetratotriamminochromate,** $4CuCrO_4.3NH_3.5H_2O$, separates as a brown, amorphous powder ; when heated, it evolves ammonia, water, and a small quantity of nitrous fumes, but the whole of the ammonia and water cannot be expelled even by heating for a long time at a high temp. It dissolves in hydrochloric acid or ammonia, forming a yellow or a green soln. respectively ; it is also easily soluble in a soln. of silver nitrate, but insoluble in organic solvents. Alcohol is not oxidized to aldehyde by boiling with the hydrochloric acid soln. of this compound. S. H. C. Briggs obtained **copper hemiheptamminochromate,** $2CuCrO_4.7NH_3.H_2O$, by pouring an aq. soln. of 14 grms. of copper carbonate and 25 grms. of chromium trioxide into a mixture of 125 c.c. conc. aq. ammonia, 50 c.c. of water, and 15 grms. of potassium hydroxide and allowing it to stand exposed to air. The greenish-black crystals lose ammonia at ordinary temp. ; they are decomposed by water ; and are soluble in dil. aq. ammonia. N. Parravano and A. Pasta prepared **copper tetramminochromate,** $CuCrO_4.4NH_3$, by adding alcohol to a soln. of copper tetrapyradinochloride in aq. ammonia ; the green prismatic crystals are decomposed by water.

L. N. Vauquelin said that when potassium " chromate " is added to a soln. of a neutral copper salt, a chestnut-brown precipitate is produced, which, according C. Gerhardt, and C. Freese, consists of $K_2O.3CuO.3CrO_3.2H_2O$, or, according to M. Gröger, $KCu_2(OH)(CrO_4)_2.H_2O$, and which, according to G. C. Gmelin, furnishes potassium dichromate when treated with boiling water. A. Bensch noticed that when potassium chromate is added to a boiling, aq. soln. of copper sulphate, the blue colour changes from green to yellow to red, and then a brown precipitate forms. B. Skormin obtained **copper trioxychromate,** $3CuO.CuCrO_4.3H_2O$, by the action of an alkaline soln. of an excess of potassium chromate on a soln. of copper sulphate. F. J. Malaguti and M. Sarzeau said that after repeated extraction with boiling water, there remains—according to the analyses of F. J. Malaguti and M. Sarzeau, J. Persoz, C. Freese, J. Schulze, L. Balbiano, M. Gröger, and M. Rosenfeld—**copper dioxychromate,** $3CuO.CrO_3.2H_2O$, or $2Cu(OH)_2.CuCrO_4$ ; and, added M. Gröger, the same product is obtained whether the potassium chromate or the copper salt be in excess. This salt was also prepared by B. Skormin. According to M. Rosenfeld, this compound is formed when potassium chromate is added to a soln. of copper sulphate ; although the colour of the substance varies with the temp. and conc. of the soln. its composition is constant. The same salt is formed by digesting freshly precipitated copper hydroxide with a soln. of potassium dichromate, but in this case it is mixed with crystals of potassium dichromate. M. Gröger said that the amorphous rust-brown precipitate, obtained by mixing aq. soln. of copper sulphate and potassium chromate, becomes crystalline when left in contact with excess of the copper salt soln. The precipitate is basic potassium cupric sulphatochromate, the proportion of sulphate present depending on the conc. of the copper salt soln. and the duration of its contact with the precipitate. The double salt is rapidly decomposed either by boiling water or by fusion, but without forming potassium chromate. The same precipitate is obtained on adding potassium hydroxide to the mixture of cupric sulphate and potassium dichromate in aq. soln. as indicated by A. Knopp. M. Gröger also said that the addition of sodium chromate to an aq. soln. of copper chloride results in the formation of a greenish-yellow precipitate which, when left in the mother-liquor, gradually assumes a bright rusty-brown colour, but does not become crystalline. The greenish-yellow substance is the basic cupric chromate, $2Cu(OH)_2,CuCrO_4$ ; the rusty-brown precipitate contains a larger proportion of chromic acid, which is removed by washing with water, the greenish-yellow salt being regenerated. According to L. Balbiano, a soln. of cupric sulphate is not completely precipitated by neutral ammonium chromate, the complete precipitation only being effected by the addition of ammonia.

Both the precipitate first produced by the ammonium chromate and that by the later addition of the ammonia have the same composition, $2CuO.CuCrO_4.2H_2O$. If the aq. soln. be evaporated on the water-bath, an amorphous mass is formed. Alcohol precipitates from the aq. soln. a dirty green precipitate, and is at the same time oxidized to acetic acid. In repeating L. Balbiano's experiments, M. Gröger observed that the original precipitate contains ammonium, and this salt furnishes the basic salt, $2Cu(OH)_2.CuCrO_4$, by washing with boiling water. A. Viefhaus obtained the same basic salt by digesting barium chromate with an aq. soln. of copper sulphate for 3 days at 30° to 35°; C. Freese, and M. Rosenfeld, by treating copper oxide or hydroxide with a boiling soln. of potassium dichromate, and extracting the product with boiling water; C. Freese, and R. Böttger, similarly treated copper carbonate with an aq. soln. of chromic acid. J. Schulze obtained this basic salt by the action of boiling water on copper chromate; and F. Dröge, by the action of boiling water on copper decamminodioxychromate. The dark brown flocculent precipitate dries at 100° to a dark brown, almost black, amorphous powder. J. Persoz said that it loses no water at 170°, but decomposes at a red-heat. F. J. Malaguti and M. Sarzeau said that it is soluble in dil. nitric acid, and in aq. ammonia. G. Gore observed that it is insoluble in liquid ammonia; R. Böttger, that it is decomposed by alkali-lye forming copper oxide; J. W. Slater, that when boiled with phosphorus, it forms copper, copper phosphide and phosphate, chromic phosphate, and phosphorus and phosphoric acids. R. Otto recommended its use in the determination of sulphur in organic analyses.

According to H. Moser, potassium dichromate does not give a precipitate with an aq. soln. of a copper salt; but, added W. E. Garrigues, if an excess of ammonia or. according to A. Kopp, and M. Rosenfeld, if sufficient potassium hydroxide be present to transform the dichromate into monochromate, a precipitate is formed which may be reddish-brown, greenish-yellow, green, or blue according to the proportion of alkali employed—the blue precipitate is copper hydroxide.

M. Rosenfeld supposed that the yellow precipitate just indicated is a basic salt *copper pentoxybischromate*, $7CuO.2CrO_3.5H_2O$; and the green precipitate, which changes to brown on drying, basic *copper hexoxychromate*, $7CuO.CrO_3.5H_2O$—probably both basic salts are mixtures of copper hydroxide and the dioxychromate. The green-coloured substance prepared by C. W. Juch by the action of 2 parts of potassium carbonate and one part of calcium carbonate on a soln. of 48 parts of copper sulphate and 2 parts of potassium dichromate; and that obtained by T. Leykauf by the action of ammonia on a soln. of 2 parts of copper sulphate and one part of potassium dichromate are also mixtures.

According to M. Vuaflart, if copper chromate be treated with aq. ammonia, the dark green soln. does not decolorize on exposure to light, and if evaporated, or cautiously treated with acids, the original chromate is restored. R. Böttger added that if the green soln. be covered with alcohol, it deposits a dark green powder, which, after washing with alcohol, furnishes, according to the analysis of F. J. Malaguti and M. Sarzeau, **copper decamminomonoxybischromate,** $CuO.2CuCrO_4.10NH_3.2H_2O$. The salt was also prepared by A. Kopp. The powder consists of dark green, acicular crystals, which lose ammonia in air: and when heated decompose with a feeble detonation. The salt is decomposed by water. According to P. A. Bolley, F. Dröge, W. Grüne, J. Stinde, and I. C. Zimmermann, the green soln. was formerly used in dyeing.

M. Gröger could not isolate **ammonium copper chromate** of definite composition; the precipitate obtained by treating copper chloride with ammonium chromate, is readily transformed into copper oxychromate. S. H. C. Briggs, and M. Gröger obtained **ammonium copper diamminochromate,** $(NH_4)_2CrO_4.CuCrO_4.2NH_3$, by the action of cupric chloride on a soln. of ammonium chromate containing an excess of ammonia; or of a soln. of copper carbonate in chromic acid on conc. aq. ammonia. The dark green crystals lose water and ammonia at 200°. The salt is hydrolyzed by water. M. Gröger mixed 2 vols. of a soln. of 85·3 grms. of $CuCl_2.2H_2O$ in a litre of water with one vol. of a soln. of 97·2 grms. of potassium chromate in a litre of water. After standing 4 days, at room temp., the precipitate was washed with

cold water by suction, and dried at 100°. The brownish-red powder consists of microscopic, four-sided, prismatic crystals of **potassium copper oxyquadrichromate,** $K_2O.4CuO.4CrO_3.3H_2O$, or $K(OH)Cu_2(CrO_4)_2.H_2O$. It is rapidly decomposed by boiling water. A. Knop reported **potassium copper oxytrischromate,** $K_2O.3CuO.3CrO_3.2H_2O$, to be formed by the action of a soln. of potassium dichromate on freshly precipitated copper hydroxide, or by gradually adding a soln. of potassium hydroxide to a mixed soln. of copper sulphate and potassium dichromate. The salt was also prepared by B. Skormin. M. Rosenfeld supposed that this product is impure copper dioxychromate, and M. Gröger, impure potassium copper oxyquadrichromate. C. Gerhardt, and C. Freese supposed the precipitate produced by potassium chromate in a cold soln. of copper sulphate to be potassium copper oxytrischromate. The pale brown powder consists of microscopic, six-sided plates. The salt loses water when heated. Boiling water extracts potassium dichromate. The salt is soluble in a soln. of ammonia and ammonium carbonate. F. Rose, S. Tschelnitz, J. G. Gentele, and G. Zerr and G. Rübencamp mentioned the use of the basic chromate as a reddish-brown pigment under the name *chrome brown.*

According to S. H. C. Briggs, **potassium copper diamminochromate,** $K_2CrO_4.CuCrO_4.2NH_3$, crystallizes out when an ammoniacal soln. of copper chromate to which a large proportion of potassium chromate has been added, is allowed to lose its free ammonia by exposure to air. The crystals were washed by decantation with the mother-liquid, then with dil. ammonia, and finally with alcohol and ether. It is slowly decomposed at 250°, rapidly at 280° ; it is decomposed by water ; and is soluble in aq. ammonia. M. Prud'homme added a cupric salt to a mixture of sodium hydroxide and chromate, and obtained a yellowish-green soln. of **sodium copper chromate.** A similar soln. is produced by boiling an excess of copper oxide with a soln. of chromic oxide in soda-lye.

According to F. Wöhler and F. Rautenberg,[8] silver chromate can be reduced to *silver subchromate,* possibly $Ag_4CrO_4$, at ordinary temp. The black powder always contains some metal ; the reduction to silver is completed at 50°. The subchromate is coloured red by nitric acid and then dissolved ; and with dil. acids a green soln. is formed. W. Muthmann showed that the alleged subchromate is a mixture of ordinary silver chromate and silver.

L. N. Vauquelin[9] obtained **silver chromate,** $Ag_2CrO_4$, by dropping a dil. soln. of potassium chromate into a conc. soln. of silver nitrate, and washing the dark reddish-brown precipitate—if the silver nitrate soln. be dropped into the chromate soln., the precipitate is orange-red, and is contaminated with the potassium salt, which is very difficult to remove by washing. N. W. Fischer found that silver oxide abstracts chromic acid from a soln. of potassium chromate leaving the liquid alkaline, but a large excess of the oxide does not remove all the chromic acid except when added in the form of its ammoniacal soln. J. Milbauer obtained a 10 per cent. conversion to chromate when a mixture of silver carbonate or oxide and chromic oxide is heated to 480° in oxygen at 12 atm. press. C. Freese obtained silver chromate by boiling silver oxide for some days with a soln. of potassium chromate or dichromate. I. Guareschi obtained silver chromate by the action of a conc. soln. of chromic acid on silver bromide ; and M. Gröger, by the action of water on ammonium silver chromate. R. Warington found that when silver dichromate is boiled with water it forms silver chromate ; according to E. Jäger and G. Krüss, and B. M. Margosches, the boiling should be continued as long as anything passes into soln. R. Warington also found that when an ammoniacal soln. of silver dichromate is evaporated spontaneously, a greenish crust of the monochromate is formed. F. A. Gooch and R. S. Bosworth showed that silver is precipitated quantitatively as chromate by adding an excess of potassium chromate to a soln. of silver nitrate. The chromate can be purified by dissolving it in aq. ammonia, and reprecipitating it by boiling the soln. G. P. Baxter and co-workers described the preparation of the salt, and added that it can be dried by heating it for 2 hrs. at 225° in a current of dry air. According to A. Lottermoser, by adding $\frac{1}{40}N$-$AgNO_3$

to an excess of $\frac{1}{40}N$-$CrO_3$, **colloidal silver chromate** is produced; the hydrosol soon becomes turbid. The Chemische Fabrik von Heyden reported that if silver chromate be formed in the presence of proteins as protective colloid, and the soln. dialyzed, or precipitated by the addition of an acid, and afterwards peptized by dil. alkali-iye, the hydrosol is stable. N. R. Dhar and A. C. Chatterji found silver chromate is not peptized by conc. soln. of cane-sugar; and N. R. Dhar and S. Ghosh that it is peptized by ammonium nitrate. N. R. Dhar and A. C. Chatterji studied the adsorption of silver ions by silver chromate. According to F. Köhler, when silver nitrate and ammonium dichromate react as a result of the diffusion which takes place when an aq. soln. of the one salt is placed in contact with a gelatinized soln. of the other, precipitation rings are formed which exhibit rhythmic character. When the ammonium salt is contained in the gelatin layer the ring formation varies with the conc. of the dichromate. At low concentrations, the rings are only partly developed, and at high concentrations they are blurred, but over an intermediate range the ring system is well developed. If the gelatin layer contains the silver salt, similar results are obtained, except that no rings are formed when the conc. is small. The conc. of the gelatin also affects the ring formation in the sense that with increasing conc. the rings become less well defined. It seems probable that rhythmic precipitation phenomena in gelatin-water systems are dependent on the existence of a more or less definite relation between the velocities of diffusion of the reacting substances and the velocity of crystallization of the products of the reaction. In the rhythmical precipitation of silver chromate by means of ammonium dichromate the small crystals of ammonium nitrate which also separate rhythmically are coloured by silver chromate, being yellowish-green to red, according to the conc. Similar coloured crystals are obtained when a soln. of ammonium nitrate containing a little ammonium dichromate is mixed with a drop of silver nitrate and allowed to evaporate on a glass slide. Exactly similar crystals are obtained when potassium dichromate is used. N. R. Dhar and co-workers supposed that the rings are produced by the coagulation of peptized silver chromate. The subject was studied by H. Bechold, H. N. Holmes, E. Hatschek, R. E. Liesegang, N. R. Dhar and A. C. Chatterji, K. C. Sen and N. R. Dhar, A. M. W. Williams and M. R. MacKenzie, T. R. Bolam and M. R. Mackenzie, G. Linck, B. Kisch, M. S. Dunin and F. M. Schemjakin, E. C. H. Davies, A. Janek, A. Steopoe, M. Storz, C. K. Jablcznysky and A. Klein, C. K. Jablczynsky, F. G. Toyhorn and S. C. Blacktin, P. B. Ganguly, R. Fricke, W. Ostwald, F. Köhler, H. McGuigan, E. R. Riegel and M. C. Reinhard, T. R. Bolam and B. N. Desal, S. S. Bhatnagar and J. L. Sehgal, L. N. Mukherjee and A. C. Chatterji, F. M. Shemjakin, H. Westerhoff, F. Pannach, H. W. Morse, W. W. Siebert, D. N. Ghosh, and S. Hedges and R. V. Henley.

Silver chromate varies in colour according to the mode of preparation, and it is described as forming tabular or acicular crystals or a dark green or purple-red crystalline powder. R. Hunt thought that the variations in colour depended on the exposure of the potassium dichromate soln. to light, for he said that the chromate produced by the actinized soln. has a "much more beautiful colour" than when produced by a soln. of dichromate which had not been exposed to light. F. Bush showed that there is no difference in the colour of silver chromate derived from insolated and non-insolated soln. of potassium dichromate, but that the rate of the mixing of the soln. determines the difference in the colour and the physical characteristics of the resulting silver chromate. C. Freese, W. Autenrieth, and B. M. Margosches found that the red variety is produced by precipitation from a silver salt with a chromate or dichromate if the silver is in excess. The result is not affected by temp. On the other hand, when silver dichromate is decomposed by cold or hot water, or when a soln. of silver chromate or dichromate is evaporated, R. Warington, E. Jäger and G. Krüss, W. Autenrieth, and B. M. Margosches observed that green crystals are produced. It has therefore been suggested that silver chromate exists in two forms: (i) red—varying from orange to deep reddish-brown; and (ii) green—varying from dark green to greenish-black, but red in

transmitted light, or in the powdered form. It has not been proved whether this is a case of polymorphism, or whether the effect is produced by the varying sizes of the crystalline granules. F. Köhler said that both silver chromate and dichromate can take small quantities of ammonium or potassium nitrate into solid soln. The colour of pure silver chromate is always greenish-black, and the red substance supposed to be a separate modification is really a mixture of silver chromate and a solid soln. of that salt with nitrates. M. Copisarow observed that tree-like, dendritic forms are produced when the precipitate is slowly formed. According to J. W. Retgers, and W. Autenrieth, the red crystals are rhombic with a pleochroism—pale reddish-brown, and brownish-black—they are not isomorphous with silver sulphate but may be so with sodium sulphate.

H. G. F. Schröder gave 5·536 for the sp. gr. of green silver chromate, and 5·523 for that of the red variety; and G. P. Baxter and co-workers gave 5·625 at 25°/4°, for the red crystals; M. L. Dundon, 5·52, and the mol. vol. 60·1 at 26°. M. L. Dundon gave 2 for the hardness, and 575 ergs per sq. cm. for the surface energy at the interface of the solid and water at 26°. According to L. N. Vauquelin, silver chromate melts in the oxidizing flame of the blowpipe; and in the inner flame, it is reduced to silver and chromic oxide. F. Kohlrausch gave for the sp. electrical conductivity of sat. soln. of silver chromate:

| | 0·26° | 14·82° | 18° | 30·76° | 37·30° | 75° |
|---|---|---|---|---|---|---|
| Conductivity . | $0{\cdot}0_5667$ | $0{\cdot}0_41561$ | $0{\cdot}0_4186$ | $0{\cdot}0_4350$ | $0{\cdot}0_4460$ | $(0{\cdot}0_3160)$ mho. |

T. R. Bolam and M. R. MacKenzie found the sp. conductivity of soln. of silver chromate and gelatine to be:

| | | | | | | |
|---|---|---|---|---|---|---|
| $Ag_2CrO_4$ . | 0·00333*N*. | 0·00250*N*- | 0·00125*N*- | 0·00236*N*- | 0·00118*N*- | 0·00162*N*- |
| Mho $\times 10^{-3}$ . | 0·8341 | 0·6841 | 0·4636 | 0·5916 | 1·3703 | 0·4207 |
| Gelatine . | 3 | 3 | 3 | 1·59 | 1·59 | 0·07 per cent. |

The conductivities are slightly smaller when the gelatine is set than when it is liquid. The electromotive force of cells with Ag | 0·1*N*-$AgNO_3$, 10*N*-$NH_4NO_3$, *x* | Ag, is 0·1483 volt when *x* is a sat. soln. of $Ag_2CrO_4$; 0·1469 volt with the same soln. with 0·01$NaNO_3$; and 0·2247 volt with the salt. soln. of silver chromate plus 0·1*N*-$K_2CrO_4$.

For the reducing action of hydrogen, *vide supra*. Silver chromate is very sparingly soluble in ammonia. Expressing the solubilities, *S*, in milligrams of silver chromate per 100 grms. of water, F. Kohlrausch gave $S=2{\cdot}52$ at 18°, from the electrical conductivity; G. S. Whitby, $S=2{\cdot}56$ at 18°, from colorimetric observations; R. Abegg and A. J. Cox, $S=2{\cdot}0$ at 25°, from potential measurements; R. Abegg and H. Schäfer, $S=2{\cdot}9$ at 25°, from the equilibrium of silver chromate and dichromate; M. S. Sherrill, $S=4{\cdot}1$ at 25°, from the solubility of silver chromate in ammonia; G. S. Whitby, $S=3{\cdot}41$ at 27°, from colorimetric observations; O. Hähnel, $S=5{\cdot}4$ at 35°, from the equilibrium with silver iodate and chromate; G. S. Whitby, $S=5{\cdot}34$ at 50°, from colorimetric observations; and R. F. Carpenter obtained $S=4{\cdot}1$ at 100°. Other observations were made by L. L. de Koninck and E. Nihoul, G. Meinecke, W. G. Young, and R. F. Carpenter. R. Abegg and H. Schäfer obtained for the solubility product $[Ag^{\cdot}]^2[CrO_4']=2{\cdot}64\times10^{-12}$ at 25°, from the equilibrium between silver chromate and dichromate. M. S. Sherrill calculated $9\times10^{-12}$ at 25°, from the solubility of silver chromate in ammonia; and O. Hähnel, $17{\cdot}7\times10^{-12}$ at 35°, from the equilibrium in the reaction $2AgIO_3'+CrO_4'' \rightleftharpoons Ag_2CrO_4+2IO_3'$. B. M. Margosches found that the solubility is diminished by the presence of $Ag^{\cdot}$-ions, or $CrO_4''$-ions, but in a conc. soln. of potassium chromate the solubility is increased. The solubility in acids is dependent on the grain-size and of the presence of silver chromate. M. L. Dundon observed a 10 per cent. increase in the solubility when the particles are reduced to 0·3$\mu$ diameter. J. Krutwig found that chlorine liberates oxygen from silver chromate at 200°, forming silver chloride and small red crystals of chromium trioxide. The relatively great solubility of silver chromate with respect to the chloride explains its use as an indicator in the titration of chlorides by a silver salt; so long as an appreciable amount of chloride

is present, silver chromate is converted into chloride, but as soon as the chloride is all consumed, the dark red colour of silver chromate appears. According to A. A. Hayes, silver chromate is decomposed by hydrochloric acid and soluble chlorides, and L. L. de Koninck and E. Nihoul said that the decomposition of the chromate by chlorides, bromides, and iodides is quantitative. B. M. Margosches found that the reaction with the alkali halides is fast only with freshly precipitated silver chromate. E. Ramann and H. Sallinger studied the system: $K_2CrO_4+AgIO_3 \rightleftharpoons KIO_3+Ag_2CrO_4$. W. R. Hodgkinson and J. Young studied the reduction of the salt by dry sulphur dioxide. A. A. Hayes found that the chromate is decomposed by soln. of sulphates. E. C. Franklin and C. A. Kraus said that silver chromate is insoluble in liquid ammonia. The chromate is slowly dissolved by cold, dil., aq. ammonia, and rapidly by hot, conc., aq. ammonia. The solubility of the chromate in aq. ammonia was measured by M. S. Sherrill, and the results expressed in $S$ mols per litre:

| $NH_4OH$ | 0·01 | 0·02 | 0·04 | 0·08 |
|---|---|---|---|---|
| $S$ | 2·04 | 4·169 | 8·595 | 17·58 |

The increased solubility with ammonia is attributed to the formation of the soluble complex $Ag(NH_3)_2CrO_4$. E. Mitscherlich, G. Meinecke, and B. M. Margosches obtained from the soln. in conc. aqua ammonia yellow tetragonal crystals of **silver tetramminochromate,** $Ag_2CrO_4.4NH_3$, with the axial ratio $a:c=1:0{\cdot}5478$. H. Topsöe gave 2·717 for the sp. gr. M. S. Sherrill's results are as follows:

| $HNO_3$ | 0·01 | 0·02 | 0·04 | 0·075 |
|---|---|---|---|---|
| $[Ag^{\cdot}]\times10^3$ | 5·808 | 7·488 | 10·02 | 12·41 |
| $[HCrO_4']\times10^3$ | 2·245 | 2·775 | 3·530 | 4·220 |
| $[Cr_2O_7']\times10^3$ | 0·3775 | 0·577 | 0·935 | 1·333 |

The tetramminochromate in air loses ammonia more rapidly than the selenate, and potash-lye precipitates fulminating silver from the aq. soln.

B. M. Margosches found that the solubility of silver chromate in nitric acid depends on the age of the salt. L. L. de Koninck and E. Nihoul measured the solubility of the chromate in nitric acid; and R. F. Carpenter, the solubility in soln. of the nitrates. M. S. Sherrill and D. E. Russ said that soln. containing more than $0{\cdot}075N$-$HNO_3$ form silver dichromate; while F. A. Gooch and R. S. Bosworth said that the chromate is insoluble in dil. nitric acid in the presence of enough potassium chromate to form with the nitric acid, dichromate and nitrate; silver chromate is also said to be insoluble in a soln. of sodium nitrate. F. A. Gooch and L. H. Weed also found the chromate insoluble in a soln. of silver nitrate; aq. soln. containing 3·24 grms. of the salt named per 100 c.c. were found to dissolve at 100° the following amounts:

| | Water | $NaNO_3$ | $KNO_3$ | $NH_4NO_3$ | $MgNO_3$ |
|---|---|---|---|---|---|
| $Ag_2CrO_4$ | 0·00415 | 0·00415 | 0·0124 | 0·0207 | 0·0166 |

B. M. Margosches said that silver chromate is practically insoluble in a soln. of silver nitrate, whilst sodium phosphate soln. form silver phosphate. Silver chromate is practically insoluble in conc. acetic acid, but some is dissolved by dil. acetic acid. A soln. of potassium chromate also dissolves a little silver chromate. A. Jaques studied the reaction with ethyl bromide. B. Guerini found that 11·65 per cent. alcohol dissolves 0·0129 grm. of silver chromate at ordinary temp. According to L. N. Vauquelin, several metals immersed in water and in contact with silver chromate exert a reducing action; and N. W. Fischer said that cadmium separates silver; zinc separates brownish-black, arborescent silver; tin, lead, and iron, a brown spongy mass; arsenic, a brown powder; copper, and mercury have a feeble action; and antimony, none. The precipitates may be contaminated with green chromic oxide; and the liquid may acquire a yellow tinge from the presence of chromic acid. With an ammoniacal soln. of silver chromate, zinc is said to precipitate silver and chromium; cadmium, silver; copper, a grey powder; lead, silver; while tin, iron, and antimony give no precipitation. C. Freese observed that a soln.

of potassium hydroxide extracts all the chromic acid from silver chromate. J. F. G. Hicks and W. A. Craig found that silver chromate undergoes a reaction with an equimolar mixture of fused potassium and sodium nitrates at about 240°, forming basic chromate analogous to a hydrolytic reaction. A state of equilibrium is established; but with fused sodium chloride, at about 870°, the reaction is complete. P. Ray and J. Dasgupta prepared a complex with hexamethylene-tetramine. S. J. Thugutt found that aragonite is coloured red whilst calcite is not changed when the minerals are treated with 0·1*N*-$AgNO_3$, and afterwards wetted with a 20 per cent. soln. of potassium dichromate.

M. Gröger obtained a precipitate by the action of an almost sat. soln. of potassium chromate on silver nitrate. The precipitate contained potassium and silver chromates, but he could not decide whether these were mechanically mixed or combined as *potassium silver chromate*. M. Gröger prepared **ammonium silver chromate,** $(NH_4)_2CrO_4.3Ag_2CrO_4$, by dropping a conc. soln. of silver nitrate into a cold, sat. soln. in ammonium chromate, and allowing the mixture to stand for some weeks; he also obtained the same salt by the action of silver nitrate on an ammoniacal soln. of ammonium chromate. The garnet-red powder or hexagonal crystals are decomposed by heat, and by water.

N. A. Orloff [10] prepared an orange-coloured soln. of **gold chromate,** $Au_2(CrO_4)_3$, by adding a soln. of auric chloride to an excess of freshly precipitated silver chromate, and filtering off the silver chloride. If the conc. soln. be evaporated in a desiccator, crystals with the composition $Au_2(CrO_4)_3.CrO_3$ are formed.

In the extraction of chromium by the calcination of a mixture of chromite and limestone, **calcium chromate,** $CaCrO_4$, is formed as an intermediate product—*vide supra*. J. Milbauer observed a 56·9 per cent. conversion to chromate when a mixture of chromic oxide and calcium oxide or carbonate is heated to 480° in oxygen at 12 atm. press. M. R. Nayer [11] and co-workers found that calcium and chromic oxides begin to interact in the presence of air to form calcium chromate at 650°; at 700°, a 95 per cent. yield of chromate is obtained with mixtures containing 2 equivalents of calcium oxide to 1 of chromic oxide and a 60 per cent. yield when the ratio is 1 : 1. In the presence of excess of calcium oxide, equilibrium is attained at about 800°, although pure calcium chromate does not begin to decompose until 1000° is reached. A mixture of calcium oxide, sodium carbonate, and chromium trioxide (1·7 : 0·65 : 1) gave a quantitative yield of chromate in 4 hrs. at 660° and in 5 minutes at 1050°. K. Herrmann and co-workers found that the crystals are rhombic bipyramids and that the crystal unit contains 4 mols, and has $a$=7·45 A., $b$=10·3 A., and $c$=5·85 A. When calcium chromate is decomposed by heat no basic salts are formed. As shown by T. Thomson, and H. Moser, a soln. of calcium chloride slowly forms a precipitate when treated with potassium dichromate; as shown by J. F. Bahr, the precipitate varies in composition, according to the conditions, from $CaCrO_4$ to $5CaCrO_4.K_2CrO_4$. If free acetic acid be present, H. Kämmerer, and F. T. Frerichs observed no precipitation; and F. Kuhlmann found that calcium carbonate is only partially converted into the chromate by a soln. of potassium chromate; lime-water gives no precipitate with a soln. of potassium chromate. F. Mylius and J. von Wrochem obtained the anhydrous chromate by heating the hydrated salt—G. N. Wyrouboff said at 300°—or by warming a supersaturated soln., containing 15 to 20 per cent. $CaCrO_4$, over 36°. The yellow powder consists of fine needles. L. Bourgeois obtained crystals of the anhydrous chromate by melting a mixture of 2 eq. of calcium chloride with an eq. each of potassium and sodium chromates. D. Vorländer and H. Hempel observed no transformation into

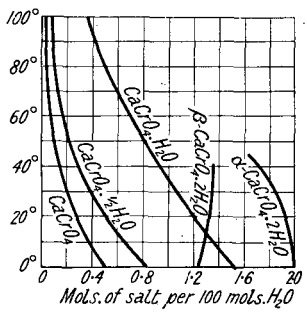


FIG. 48. — The Solubility Curves of Calcium Chromate.

an isotropic form when the alkaline earth chromates are heated. The sat., aq. soln. at 18° has a sp. gr. 1·023 and contains 2·3 per cent. $CaCrO_4$. It is very stable, and is not hydrated by standing for a year in contact with water. Three hydrates have been reported. The percentage solubility, $S$, of stable $CaCrO_4$ is :

| | 0° | 20° | 30° | 50° | 70° | 100° |
|---|---|---|---|---|---|---|
| $S$ | 4·31 | 2·23 | 1·92 | 1·11 | 0·80 | 0·42 |

The results are plotted in Fig. 48. By mixing a 15 per cent. soln. of calcium chromate with calcium chloride or glycerol, and rapidly warming to 100°, small, doubly refracting, presumably rhombic crystals of the *hemihydrate*, $CaCrO_4.\frac{1}{2}H_2O$, are formed. They lose water at 400° ; and a soln., sat. at 18°, has 4·4 per cent. $CaCrO_4$, and a sp. gr. of 1·044. The percentage solubility, $S$, of the unstable hemihydrate, Fig. 48, is :

| | 0° | 18° | 30° | 50° | 70° | 100° |
|---|---|---|---|---|---|---|
| $S$ | 6·80 | 4·4 | 3·66 | 1·60 | 1·10 | 0·80 |

According to H. von Foullon, the *monohydrate*, $CaCrO_4.H_2O$, is produced when the mother-liquor from the dihydrate is evaporated over 25° ; and F. Mylius and J. von Wrochem obtained it by heating the rhombic $\beta$-dihydrate at 12°. The orange-red, rhombic, bipyramidal crystals were found by F. von Foullon to have the axial ratios $a : b : c = 0{\cdot}6296 : 1 : 0{\cdot}6404$. G. N. Wyrouboff gave $0{\cdot}9917 : 1 : 0{\cdot}7995$ and said that the crystals are similar to those of anhydrite. The sp. gr. is 2·793 at 15°, and the mol. vol. 62·4. F. Mylius and J. von Wrochem said that the dark yellow, four-sided, doubly refracting pyramids do not effloresce very much at ordinary temp. The soln. sat. at 18° has a sp. gr. 1·096, and contains 9·6 per cent. of $CaCrO_4$. The percentage solubility, $S$, Fig. 48, of the unstable monohydrate, is

| | 18° | 25° | 40° | 60° | 75° | 100° |
|---|---|---|---|---|---|---|
| $S$ | 9·60 | 9·09 | 7·83 | 5·75 | 4·58 | 3·10 |

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J. F. Bahr said that when calcium carbonate is treated with a soln. of chromic acid, the dihydrate, $CaCrO_4.2H_2O$, is formed ; and M. Siewert obtained the dihydrate by evaporating in vacuo a soln. of the carbonate in chromic acid. H. von Foullon said that the dihydrate exists in two forms. There is first the labile or *α-dihydrate* obtained by the slow evaporation below 25° of the mother-liquid from the basic salt, or up to 65° in the presence of sulphuric acid. F. Mylius and J. von Wrochem observed that it separates from a supersaturated soln. of calcium chromate at room temp. The sulphur-yellow, monoclinic crystals resemble those of the dihydrated calcium sulphate. There is the stable or $\beta$-dihydrate obtained by allowing the $\alpha$-form to stand in contact with a sat. soln. of calcium chromate ; it also separates when the sat. soln. is allowed to stand for a week. H. von Foullon obtained crystals by evaporating a soln. at 22°. A. Fock also described the preparation of the dihydrate, and according to A. Fock, and H. von Foullon, the pale yellow, rhombic crystals do not resemble those of gypsum. The axial ratios are $a : b : c = 0{\cdot}6942 : 1 : 0{\cdot}7388$. The (100)-cleavage is complete. G. N. Wyrouboff could not prepare the dihydrate. M. Siewert said that the dihydrate loses its water when strongly heated, and every time it is heated it becomes cinnabar-red. F. Mylius and J. von Wrochem found that the $\beta$-dihydrate at 12° forms the monohydrate. At 18°, the sat. aq. soln. of the $\alpha$-form contains 14·3 per cent. of $CaCrO_4$ and has a sp. gr. of 1·149 ; while with the $\beta$-form there is present 10·3 per cent. of $CaCrO_4$ and the sp. gr. is 1·105. M. Siewert, and H. Schwarz made observations on the solubility. F. Mylius and J. von Wrochem found that the percentage solubilities, $S$, Fig. 48, are :

| | $\alpha$-dihydrate | | | $\beta$-dihydrate | | |
|---|---|---|---|---|---|---|
| | 0° | 20° | 45° | 0° | 20° | 40° |
| $S$ | 14·70 | 14·20 | 12·40 | 9·83 | 10·20 | 10·40 |

The transition temp. for $\beta$-dihydrate$\rightleftharpoons$monohydrate is 10·20° with 14 per cent.

$CaCrO_4$. F. Kohlrausch measured the electrical conductivity of aq. soln. of the salt, while H. H. Hosford and H. C. Jones found for the mol. conductivity, $\mu$ mhos, between 0° and 35°, and S. F. Howard and H. C. Jones between 35° and 65°, the following values, when a mol of the salt is dissolved in $v$ litres :

| | $v$ | 8 | 16 | 32 | 128 | 512 | 1024 | 2048 | 4096 |
|---|---|---|---|---|---|---|---|---|---|
| $\mu$ | 0° | 62 | 69 | 77 | 97 | 114 | 119 | — | 124 |
| | 12·5° | 86 | 96 | 108 | 135 | 160 | 168 | — | 173 |
| | 25° | 113 | 126 | 142 | 179 | 212 | 223 | — | 230 |
| | 35° | 134 | 147 | 169 | 214 | 255 | 270 | — | 279 |
| | 65° | 200 | 229 | 260 | 337 | 412 | 428 | 288 | — |
| $\alpha$ | 0° | 49·70 | 85·64 | 62·19 | 78·55 | 91·90 | 96·12 | 98·54 | 100·00 |
| | 65° | 65·02 | — | 77·01 | 86·41 | 93·19 | 96·18 | 97·60 | 100·00 |

The percentage ionization, $\alpha$, has also been calculated.

H. Caron and D. A. Raquet found dihydrated calcium chromate to be soluble in acids and in dil. alcohol. C. R. Fresenius found that 100 c.c. of 29 per cent. alcohol dissolve 1·216 grms. calcium chromate, and 100 c.c. of 53 per cent. alcohol, 0·88 grm. The anhydrous salt is insoluble in absolute alcohol ; and A. Naumann observed that it is insoluble in acetone. F. Guthrie observed that molten sodium nitrate dissolves 0·547 grm. of the salt. J. F. G. Hicks and W. A. Craig found that equimolar mixture of fused sodium and potassium nitrates, at about 870°, reacts with calcium chromate forming basic salts and entering into a state of equilibrium analogous to a hydrolytic reaction. L. Kahlenberg and W. J. Trautmann found that when calcium chromate is mixed with silicon and heated in the electric arc furnace there is a strong reaction, but in the bunsen burner there is a slight reaction. J. B. Hannay obtained *potassium calcium sulphatochromates*, $K_2CrO_4.CaSO_4,H_2O$ ; $2K_2CrO_4.CaSO_4$ ; and $K_2CrO_4.CaSO_4.Na_2SO_4.H_2O$. H. von Foullon obtained the basic salt, **calcium oxychromate,** $CaO.CaCrO_4.3H_2O$, by warming to 50°–60°, a soln. of calcium carbonate in a dil. aq. soln. of chromic acid ; or, according to F. Mylius and J. von Wrochem, from a soln. of chromic acid supersaturated with calcium hydroxide. The lemon-yellow, monoclinic prisms have the axial ratios $a : b : c = 1·0311 : 1 : 0·6500$, and $\beta = 98°\ 13'$. 100 parts of water dissolve 0·435 part of the salt.

K. S. Nargund and H. E. Watson found that when calcium chromate is heated to 1030° at less than 20 mm. press., **calcium dichromitochromate,** $3CaO.Cr_2O_3.CrO_3$, is formed ; if the press. be 2 mm., **calcium hexachromito*bis*chromate,** $8CaO.3Cr_2O_3.2CrO_3$, is produced ; and at lower press., **calcium tetrachromitochromate,** $5CaO.2Cr_2O_3.CrO_3$, results, and it has no measurable dissociation press. at 1030°. If calcium chromate mixed with lime is heated, **calcium oxy*bis*chromate,** $CaO.2CaCrO_4$, is formed, and it readily decomposes, forming **calcium dichromito*sexies*chromate,** $12CaO.Cr_2O_3.6CrO_3$, with a dissociation press. of 270 mm. at 910° ; and it decomposes, forming **calcium dichromito*quater*chromate,** $9CaO.Cr_2O_3.4CrO_3$, with a dissociation press. of 22 mm. at 920°. This product is also formed when a mixture of calcium oxide and chromate is heated in air ; the black compound is soluble in dil. acids, and when heated to 1030° furnishes **calcium dichromito*tris*chromate,** $6CaO.Cr_2O_3.3CrO_3$. A mixture of calcium chromate and chromic oxide yields **calcium dichromito*bis*chromate,** $2CaO.Cr_2O_3.2CrO_3$, with a dissociation press. of 150 mm. at 1030°, and finally a chromite.

A. Duncan found that a soln. of freshly burnt lime in an aq. soln. of potassium dichromate, when evaporated, gives orange-yellow crystals of **potassium calcium chromate,** $K_2CrO_4.CaCrO_4$, which are the *monohydrate* if the crystallizing soln. is boiling, and the *dihydrate*, if the soln. is at 80°. E. Schweizer obtained the dihydrate by saturating a not too conc. soln. of potassium dichromate with calcium hydroxide, passing a current of carbon dioxide through the clear liquid, and evaporating the soln. at 30°–40°. The crystals of the dihydrate are lemon-yellow. There is formed at the same time a brown crystalline crust of $K_2CrO_4.4CaCrO_4.2H_2O$, which is easily separated from the lemon-yellow crystals of the dihydrate. M. Gröger obtained it by evaporating on a water-bath an almost sat. soln. of potassium chromate containing 4 eq. of $N$-$CaCl_2$. M. Barre found that by the direct action of calcium chromate on soln. of potassium chromate at temp. below 45°, large rhombic prisms of the salt $K_2CrO_4.CaCrO_4.2H_2O$ are obtained. These, in contact

with a soln. of potassium chromate at 60°, slowly disappear, and small, hexagonal prisms of the anhydrous salt, $K_2CrO_4.CaCrO_4$, are formed. Both these salts are decomposed by water. F. Stolba, and F. Mohr made some observations on this salt. G. N. Wyrouboff said that the crystals are dimorphous since there is an $\alpha$-form occurring in yellow triclinic pinacoids $a:b:c=0{\cdot}6591:1:0{\cdot}4383$, and $\alpha=78°\ 16'$, $\beta=101°\ 3'$, and $\gamma=83°\ 8'$. The (101)-cleavage is complete, and the $(10\bar{1})$-cleavage is distinct. The sp. gr. is 2·411 at 15°, and the mol. vol. 160·5. The brown $\beta$-form also occurs in triclinic pinacoids with the axial ratios $a:b:c=0{\cdot}7516:1:0{\cdot}8807$, and $\alpha=86°\ 0'$, $\beta=94°\ 41'$, and $\gamma=81°\ 37'$. The (010)-cleavage is nearly complete. The sp. gr. is 2·596 at 15°, and the mol. vol. 149·3. The $\alpha$-form is produced before the $\beta$-form. A. Rakowsky said that the $\alpha$-form is not stable above 20°, and G. N. Wyrouboff added that it begins to give off water at 100°, and is completely dehydrated at 120°. A. Rakowsky found that the $\alpha$-variety is less soluble than the $\beta$-form. Water at 0° and 15° dissolves respectively 23·06 and 25·06 parts of the $\alpha$-form, and respectively 23·01 and 24·45 parts of the $\beta$-form. The heats of soln. of the $\alpha$- and $\beta$-forms are, respectively, —6·99 Cals. and —5·45 Cals. H. G. F. Schröder gave 2·502 for the sp. gr. of the salt. E. Schweizer said that the salt loses water when heated, and becomes reddish-yellow while hot. It melts at a dull red-heat and forms, when cold, a crystalline cake. A. Duncan said that the salt which has been fused dissolves readily in water, but not in alcohol; and M. Gröger added that the salt is soluble in cold water without decomposition. E. Schweizer found that the aq. soln. decomposes on evaporation forming $K_2CrO_4.4CaCrO_4.2H_2O$. According to E. Schweizer, **potassium calcium quinquemonochromate,** $K_2CrO_4.4CaCrO_4.2H_2O$, is obtained, as indicated above. H. G. F. Schröder gave 2·787 for the sp. gr. In addition to the *dihydrate*, G. N. Wyrouboff obtained yellow *hemiheptahydrate*, $K_2CrO_4.4CaCrO_4.3\frac{1}{2}H_2O$, by saturating a cold, conc. soln. of potassium dichromate with calcium oxide, and allowing the filtered soln. to stand over sulphuric acid in a warm place. J. F. Bahr found that **potassium calcium seximonochromate,** $K_2CrO_4.5CaCrO_4$, separated during the evaporation of a soln. of calcium chloride and potassium chromate. The yellow, granular salt decrepitates when heated, and dissolves in water. M. Gröger could not prepare **ammonium calcium chromate.**

A. Osann found in the caliche deposits of Atacama, Chili, a salt which had a composition corresponding with **calcium iodatochromate,** $7Ca(IO_3)_2.8CaCrO_4$, and the mineral was called **dietzeite**—after A. Dietze, who had previously observed the complex salt in the same deposit. B. Gossner and F. Mussgnug's examination showed that the composition approximates $Ca(IO_3)_2.CaCrO_4$, and B. Gossner considered that the iodate and chromate furnish isomorphous mixtures. According to A. Osann, the colour of dietzeite is golden-yellow. The crystals are prismatic and tabular; but the mineral is commonly fibrous to columnar. The axial ratios of the monoclinic crystals are $a:b:c=1{\cdot}3826:1:0{\cdot}9515$, and $\beta=73°\ 28'$. B. Gossner and F. Mussgnug found that the X-radiograms correspond with $a=10{\cdot}6$ A., $b=7{\cdot}30$ A., $c=14{\cdot}03$ A., and $\beta=106°\ 32'$. This gives the axial ratios $a:b:c=1{\cdot}392:1:1{\cdot}922$; the elementary cell has the volume $997\times10^{-24}$ c.c. According to A. Osann, the (100)-cleavage is imperfect; the lustre is vitreous; and the fracture, conchoidal. The optical character is positive and the optical axial angle $2G=87°$ to 88°. The hardness is 3 to 4; and the sp. gr. 3·698. B. Gossner and F. Mussgnug calculated 3·617 for the sp. gr. The salt is soluble in hot water, and the soln., on cooling, deposits crystals of $Ca(IO_3)_2.6H_2O$.

When a soln. of strontium chloride is treated with potassium chromate, **strontium chromate,** $SrCrO_4$, is precipitated. J. D. Smith observed that no precipitation occurs with dil. soln.; J. W. Döbereiner, that aq. soln. of strontium hydroxide gave no precipitate; and H. Kämmerer, and F. T. Frerichs, that no precipitation occurs if the soln. be acidified with acetic acid, but H. Caron and D. A. Raquet found that if the soln. be neutralized with ammonia, and treated with alcohol, strontium chromate is precipitated. A. de Schulten obtained the crystalline

salt by dissolving 25 grms. of $Sr(HO)_2.4H_2O$ and 30 grms. of potassium dichromate in 100 c.c. of water heated on a water-bath, and adding drop by drop 0·3 per cent. ammonia. L. Bourgeois obtained the crystalline salt by melting a mixture of strontium chloride and sodium and potassium chromates as in the case of the calcium salt. The pale yellow powder consists of monoclinic prisms or plates which, according to A. de Schulten, have the axial ratios $a : b : c = 0{\cdot}9666 : 1 : 0{\cdot}9173$, and $\beta = 102° 43'$. E. Herlinger studied the structure of the crystals; and L. Bourgeois said that they are isomorphous with those of barium and calcium chromates, and with the sulphate. W. Autenrieth observed that strontium chromate furnishes bundles of long, slender, highly refracting needles, or, when separating from very dil. soln., it furnishes thick prisms of hexagonal habit. The latter appears to be a labile form which is slowly converted into the former. H. G. F. Schröder gave 3·353 for the sp. gr., and A. de Schulten, 3·895 at 15°. According to C. R. Fresenius, 100 parts of water at 15° dissolve 0·12 part of strontium chromate; and I. Meschtschersky, 0·119 part at 16°. F. Kohlrausch found that 100 c.c. of a soln. at 18° contain 0·12 grm. $SrCrO_4$; and C. Reichard, that water at 10° dissolves 0·465 per cent.; at 20°, 1·000 per cent.; at 50°, 2·417 per cent.; and at 100°, 3·000 per cent. F. Ransom made some observations on this subject. H. Caron and D. A. Raquet said that the solubility in water is lowered by the addition of alcohol. C. Reichard found that the chromate is freely soluble in hydrochloric, nitric, or aq. chromic acids; W. Autenrieth, and H. Caron and D. A. Raquet, that it is freely soluble in acetic acid—I. Meschtschersky said sparingly soluble. C. R. Fresenius observed that 100 c.c. of 29 per cent. alcohol dissolve 0·0132 grm. of strontium chromate; and 100 c.c. of 53 per cent. alcohol, 0·002 grm. E. Dumesnil said that it is readily soluble in a soln. of ammonium chloride, so that 100 c.c. of a sat. soln. of ammonium chloride, on boiling, easily dissolve a gram of the chromate. C. R. Fresenius observed that 100 parts of a 0·5 per cent. soln. of ammonium chloride at 15° dissolve 0·195 part of strontium chromate; 100 parts of 1 per cent. acetic acid, 1·57 part; and 100 c.c. of 0·75 per cent. acetic acid mixed with a little ammonium chromate, dissolve 0·287 part. F. Guthrie added that molten sodium nitrate dissolves 2·133 per cent. of strontium chromate. Strontium chromate has been used as a pigment—*lemon-yellow, strontian yellow, jaune de strontiane, giallo di stronziana,* and *amarillo di estronciana.*

M. Gröger prepared **potassium strontium chromate,** $K_2CrO_4.SrCrO_4$, by the action of an almost sat. soln. of potassium chromate containing 4 eq. of *N*-$SrCl_2$. M. Barre also prepared this salt. The yellow crystals are decomposed by water into the constituent salts. M. Barre found that the complex salt is stable at 11·5° in contact with a soln. containing 2·914 parts of potassium chromate per 100 parts of water; at 27·5°, 4·123 parts; at 50°, 5·942 parts; at 76°, 7·920 parts; and at 100°, 9·784 parts. He also obtained **ammonium strontium chromate,** $(NH_4)_2CrO_4.SrCrO_4$, by the action of a soln. of strontium chloride on one of ammonium chloride. The pale yellow crystals are decomposed by water.

When an aq. soln. of a barium salt, or baryta-water is treated with alkali mono- or di-chromate, a pale yellow precipitate of **barium chromate,** $BaCrO_4$, is deposited. J. D. Smith said that the precipitation with a barium salt is as delicate a test for chromate as it is for sulphates. F. T. Frerichs, and H. Kämmerer obtained a complete precipitation in the presence of acetic acid or sodium acetate. P. D. Chrustschuff and A. Martinoff observed that 12 per cent. of barium sulphate is converted into barium chromate by contact for 47 min. with a soln. containing potassium sulphate and potassium chromate in eq. proportions, whilst 1·5 per cent. of barium chromate is converted into barium sulphate in the same time in contact with a similar soln. The limits of the reaction do not attain more than 22 per cent. and 17 per cent. respectively, even after 40 to 45 hrs. M. Scholtz and R. Abegg found that at 100°, equilibrium between barium sulphate and potassium chromate in aq. soln. is established very slowly; it is reached more rapidly when a soln. of potassium sulphate acts on barium chromate. The ratio between the quantities

of potassium chromate and sulphate in soln. when equilibrium is reached depends on the relative quantities of the solid barium salts, from which it appears that the precipitate consists of a solid soln. The relation $[K_2CrO_4][K_2SO_4] = 1{\cdot}3[BaCrO_4][BaSO_4]$ appears to hold. H. Rose found that an excess of alkali chromate will completely transform barium carbonate into the chromate; and F. J. Malaguti made observations on this subject, and J. Morris studied the precipitation of barium from a soln. of its chloride by the addition of a mixture of potassium carbonate and chromate. M. Scholtz and R. Abegg showed that in the equilibrium between potassium chromate and barium carbonate, the ratio of the conc. of potassium carbonate and chromate also varies in the same way as the ratio between the numbers of mols. of barium carbonate and chromate in the precipitate, but the two ratios are not proportional. There is, however, always relatively less chromate in the soln. than in the precipitate. Barium chromate and sulphate are about equally soluble, and both are much less soluble than the carbonate. A. Pool also studied this system. J. F. Bahr obtained crystalline barium chromate by decomposing barium dichromate with water; A. de Schulten, by heating on a water-bath a soln. of 20 grms. of barium nitrate in a litre of water mixed with 10 c.c. of nitric acid of sp. gr. 1·2, and adding 2 litres of a soln. of 10 grms. of potassium dichromate; and L. Bourgeois by melting 2 eq. of barium chloride with one eq. each of sodium, and potassium chromates. J. Milbauer found that when a mixture of barium oxide or carbonate and chromic oxide is heated to 480° in oxygen at 12 atm. press. there is a 52·8 per cent. conversion to chromate. J. A. Atanasiu found that in the electrometric titration of soln. of barium chloride soln. and potassium chromate there is a break corresponding with normal barium chromate. O. Ruff and E. Ascher studied the joint precipitation of lead and barium chromates; barium and strontium chromates; and barium sulphate and chromate; and O. Ruff, the X-radiograms.

The pale lemon-yellow barium chromate was found by H. Moser to become dark yellow when heated. L. Bourgeois said that the rhombic prisms are isomorphous with barium sulphate; and A. de Schulten gave for the axial ratios of the rhombic plates $a : b : c = 0{\cdot}8038 : 1 : 1{\cdot}2149$. F. Rinne studied the crystals of barium chromate; and M. Copisarow observed tree-like, dendritic forms are produced when the precipitate is slowly formed. The sp. gr. observed by H. G. F. Schröder is 4·296–4·304; C. H. D. Bödecker, 3·90 at 11°; E. Schweizer, 4·5044; A. Schafarik, 4·49 at 23°; L. Bourgeois, 4·60; and A. de Schulten, 4·498 at 15°. P. Bary, and J. Precht found that the salt is not fluorescent when exposed to X-rays. F. Kohlrausch gave for the sp. conductivity of sat. soln. $0{\cdot}0_5114$ mho at −0·88°; $0{\cdot}0_5297$ mho at 16·07°, $0{\cdot}0_5317$ mho at 17·42°; and $0{\cdot}0_5499$ mho at 28·08°. The solubility of the salt in water is very small; F. Kohlrausch and co-workers calculated from observations on the electrical conductivity, the following solubilities, $S$ grms. per litre:

| | −0·88 | 16·07° | 17·42° | 18° | 28·08° |
|---|---|---|---|---|---|
| $S$ . . | 2·04 | 3·37 | 3·48 | 3·53 | 4·36 |

For the equilibrium between barium chromate and dichromate, *vide supra*, chromic acid. I. Meschtschersky found that a litre of water dissolved 4·3 mgrms. at 100°. C. R. Fresenius said that at 0°, a litre of water dissolves 1·19 mgrms. The salt is less soluble after it has been ignited. E. Schweizer said that in that state a litre of water dissolves 0·62 mgrm. L. M. Henderson and F. C. Kracek pointed out that the solubilities of the alkaline earth chromates decrease as the at. wt. of the alkaline earth metal. Thus, at 15°, the solubilities of the anhydrous calcium, strontium and barium chromates are of the order 25, 1·2, and 0·0033 grms. per litre respectively. The solubility of **radium chromate** seems to follow the rule, and a separation of radium and barium can be effected by fractional precipitation as chromates. The partition factor for acidic soln. is about 15·5.

The soln. of barium chromate in hydrochloric, or nitric acid or in an excess

of chromic acid, was found by J. F. Bahr, H. Caron and D. A. Raquet, and K. Preis and B. Rayman to become orange-red owing to the formation of dichromate, but the monochromate is reprecipitated from this soln. by ammonia. The statement with reference to the solubility in soln. of chromic acid was disputed by L. Schulerud, and W. Autenrieth. E. Schweizer said that the salt is insoluble in a soln. of potassium dichromate, and 100 parts of a 10 per cent. soln. of chromic acid dissolve 0·055 part of chromate. When sulphur dioxide is passed over heated barium chromate W. R. Hodgkinson and J. Young found that chromium sulphate is formed as the chromate is decomposed. N. W. Fischer observed that barium chromate is not decomposed by cold sulphuric acid, but is decomposed with difficulty by the hot acid; he also stated that aq. soln. of sulphates do not affect the chromate, and the action is only slight with hot soln. H. Schwarz found that about a quarter mol is decomposed by a mol of conc. sulphuric acid to form, according to L. Bourgeois, barium sulphate and chromium trioxide. Observations by P. D. Chrustschoff and A. Martinoff, M. Scholtz and R. Abegg are indicated above. The transformation of the chromate into carbonate by the fusion with sodium carbonate, or by digestion with a soln. of the carbonate, was discussed by H. Rose, F. J. Malaguti, M. Scholtz and R. Abegg—*vide supra*. K. W. Flöroff gave $1{\cdot}6\times10^{-11}$ for the solubility product at 18°. According to H. Golblum, the equilibrium constant $K=[K_2CO_3]/[K_2CrO_4]$ in the reaction: $K_2CO_3+BaCrO_4\rightleftharpoons BaCO_3+K_2CrO_4$, is not constant but decreases to a minimum value. The deviation from the simple mass law is ascribed to the ionization of the salts. The heat of the reaction, calculated from the equilibrium constants at 25° and 40°, is 5997 cals. E. Carrière and P. Castel found that the equilibrium constant $K=[CrO_4]^2[H]^2/[Cr_2O_7]$ with barium chromate in acid soln. is $3\times10^{-15}$.

B. Guerini observed that $0{\cdot}22\times10^{-4}$ gram-equivalent of barium chromate are dissolved by a litre of 45 per cent. alcohol, and A. Naumann observed that it is insoluble in acetone, and in methyl acetate. I. Meschtschersky, and H. Baubigny said that the chromate is soluble in acetic acid; while H. Caron and D. A. Raquet said that barium chromate is insoluble in acetic acid and soln. of alkali chromate, but partially soluble in a mixture of dichromate and acetic acid. According to C. R. Fresenius, the presence of acetic acid increases the solubility of barium chromate, for 100 parts of water containing one part of acetic acid dissolve 0·0027 part of chromate. E. Schweizer said that 100 parts of 5 per cent. acetic acid dissolve 0·02725 part of chromate, and with 10 per cent. acetic acid, 0·0503 part. C. R. Fresenius said that ammonium salts also make the chromate more soluble, thus 100 parts of water containing 0·5 per cent. of ammonium chloride dissolve 0·00435 part of the chromate; water with 0·5 per cent. of ammonium nitrate dissolves 0·00222 part of chromate; water with 0·75 per cent. of ammonium acetate dissolves 0·002 part of chromate; and water with 1·5 per cent. of ammonium acetate dissolves 0·00417 part of chromate. E. Fleischer found that barium chromate is readily soluble in soln. of alkali tartarate or citrate; L. Bourgeois that it is decomposed with difficulty by alkali hydroxides; and F. Guthrie that molten sodium nitrate dissolves 0·205 per cent. $BaCrO_4$. K. W. Flöroff studied the adsorption of potassium chromate by barium sulphate, and showed that the reaction, particularly for conc. soln., is complex—probably $2BaSO_4+K_2CrO_4=BaSO_4.BaCrO_4+K_2SO_4$. L. Kahlenberg and W. J. Trautmann observed that when mixed with silicon, there is a strong reaction at a cherry-red-heat, and in the electric arc. C. Zerr and G. Rübencamp mentioned the use of barium chromate as a pigment—*ultramarine yellow, lemon yellow, permanent yellow, jaune de baryte, giallo di barite, amarillo di barita, oltremare giallo, outremer jaune, amarillo ultrames, Citrongelb*. M. A. Iljinsky and co-workers studied the adsorption of barium chromate by silk, wool, and cotton fibres.

M. Gröger prepared **potassium barium chromate,** $K_2CrO_4.BaCrO_4$, by shaking an almost sat. soln. of potassium chromate with a cold, sat. soln. of barium chloride. The pale yellow granules are decomposed by water. M. Barre also prepared this

salt. M. Gröger also made **ammonium barium chromate** by precipitation with soln. of ammonium chromate and barium chloride. The precipitate is at first amorphous, but soon forms six-sided plates. The salt is decomposed by water. L. Bourgeois reported **barium strontium chromate,** $BaSr(CrO_4)_2$, to be formed in prismatic crystals by the process used for strontium calcium chromate—*vide supra ;* similarly also with **barium calcium chromate,** $BaCa(CrO_4)_2$. L. H. Duschak found that a crystalline precipitate of barium and strontium chromates of definite composition is formed in a sat. soln. of barium chromate containing given conc. of strontium chromate and acetic acid. Diffusion takes place within this substance, and that, therefore, it must either be regarded as a solid soln., or else diffusion must be recognized as a possible property of isomorphous mixtures. L. M. Henderson and F. C. Kracek [12] discussed the separation of radium and barium by the fractional precipitation of barium chromate and **radium chromate.**

A. Atterberg [13] found that beryllium hydroxide dissolved in an aq. soln. of chromic acid to form a deep red liquid from which no crystals can be obtained ; and that when a soln. of beryllium sulphate is treated with potassium chromate, the precipitate first formed dissolves with stirring, and finally there is deposited a yellow basic salt. J. C. G. de Marignac treated soln. of potassium dichromate with beryllium sulphate and obtained a precipitate of variable composition. A. Atterberg found that beryllium carbonate is decomposed by a soln. of potassium dichromate, carbon dioxide is evolved, and a basic chromate is formed. This when washed and dried gives a pale yellow powder approximating $14BeO.CrO_3.23H_2O$. It loses 5 mols. of water at 100° ; 16 mols. at 300° ; and all is lost at dull redness. At a higher temp. oxygen is given off. B. Glassmann obtained **beryllium dodecahydroxychromate,** $6Be(OH)_2.BeCrO_4$, as a yellow powder by heating the normal chromate with water, or by treating a soln. of beryllium sulphate with ammonium chromate. It is insoluble in water, but soluble in chromic acid soln. Normal **beryllium chromate,** $BeCrO_4.H_2O$, was obtained by neutralizing a conc. soln. of chromic acid with beryllium carbonate, and evaporating the liquid. The reddish-yellow, monoclinic plates are hydrolyzed by water. B. Bleyer and A. Moormann could not obtain either of the two salts described by B. Glassmann. The precipitation of beryllium sulphate by potassium chromate yields impure, amorphous products of varying composition, whilst the precipitate from the chloride has the composition $15BeO.CrO_3.12H_2O$, independently of the proportions of the reacting substances. Beryllium hydroxide and chromic acid yield only resinous masses, but the clear soln. contains beryllium and chromium in the ratio 1 : 1. N. A. Orloff obtained $9BeO.BeCrO_4.16H_2O$ and $20H_2O$, and $14BeO.BeCrO_4.31H_2O$, from a soln. of beryllium sulphate and potassium chromate ; $12BeO.BeCrO_4.16H_2O$ from a soln. of beryllium hydroxide in chromic acid and potassium chromate ; and $5BeO.BeCrO_4.14H_2O$, as a precipitate by adding alcohol to a soln. of beryllium hydroxide in chromic acid. Hence, beryllium chromate is gradually hydrolyzed by water without forming any definite basic salt. H. C. Creuzberg prepared beryllium tridecoxychromate, $BeCrO_4.13BeO.23H_2O$, by precipitation.

L. N. Vauquelin [14] prepared **magnesium chromate,** $MgCrO_4$, by crystallization from a soln. of magnesia in chromic acid. J. Milbauer observed an 82·7 per cent. conversion to chromate when chromic oxide mixed with magnesium oxide or carbonate is heated to 480° in oxygen at 12 atm. press. The orange-yellow, six-sided prisms of the chromate crystallized in aq. soln. were said by H. Kopp to be isomorphous with magnesium sulphate, and his analysis corresponded with *heptahydrate,* $MgCrO_4.7H_2O$. A. Murmann gave for the axial ratios of the rhombic, bisphenoidal crystals $a : b : c = 0·9901 : 1 : 0·5735$. The (010)-cleavage is perfect. W. J. Grailich gave for the optic axial angle $2V = 75° 28'$. The optical character is negative. E. Dittler obtained overgrowths with magnesium sulphate. H. G. K. Westenbrink found that the rhombic bisphenoidal crystals have four mols. in unit cell, and that the dimensions are $a = 11·89$ A., $b = 12·01$ A., and $c = 6·89$ A. Observations on the crystals were made by H. Dufet, and L. Longchambon ;

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C. Gaudefroy studied the corrosion figures; and A. Fock, the solid soln. of the heptahydrates of magnesium chromate and sulphate. H. Kopp gave 1·66 for the sp. gr. at 15°; C. H. D. Bödeker, 1·75; and F. W. Clarke, 1·761 at 16°. F. Mylius and R. Funk observed that a sat. soln. containing 4·2 per cent. $MgCrO_4$ had a sp. gr. 1·422; A. Heydweiller found the sp. gr. at 18°/18° of soln.:

| $MgCrO_4$ . | 0·1234*N*- | 0·247*N*· | 0·617*N*· | 1·1234*N*- | 2·468*N*- | 4·936*N*- |
|---|---|---|---|---|---|---|
| Sp. gr. . | 1·00857 | 1·01710 | 1·04178 | 1·0818 | 1·1596 | 1·3052 |

K. F. Slotte found the sp. gr. of soln. of magnesium chromate with 12·31, 21·86, and 27·71 per cent. of chromate to be respectively 1·0886 at 13·6; 1·1641 at 14·5°; and 1·217 at 13·6°; and the viscosities (water 100) to be respectively 151·8, 227·8, and 317·7 at 10°; 115·4, 170·9, and 235·6 at 20°; 92, 134·7, and 182·8 at 30°; and 75, 108·6, and 145·5 at 40°. W. Kohlrausch said that 100 c.c. of a sat. soln. at 18° contain 60 grms. $MgCrO_4$; and G. N. Wyrouboff found that the heptahydrate lost 2 mols. of water in air, 3 mols. at 120°; but expulsion of the last mol. of water is attended by the decomposition of the salt. M. R. Nayar and co-workers observed that very little chromate is formed when a mixture of magnesia and chromic oxide is heated below 600°; at 650°, magnesium chromate decomposes into basic chromites (*q.v.*). H. Topsöe and C. Christiansen found the indices of refraction for the *D*-line to be $\alpha=1{\cdot}5211$, $\beta=1{\cdot}5500$, and $\gamma=1{\cdot}5680$; while for the *C*-line, $\alpha=1{\cdot}5131$, $\beta=1{\cdot}4315$, and $\gamma=1{\cdot}5633$. A. Fock gave for the refractive indices, $\mu$, and the optic axial angle, $2V$, of mixtures of magnesium sulphate and chromate containing the eq. per cent. of $MgCrO_4.7H_2O$,

| $MgCrO_4.7H_2O$ | | 0 | 52 | 15·8 | 18·5 | 31·6 | 35·9 | 43·7 | 100 per cent. |
|---|---|---|---|---|---|---|---|---|---|
| $\mu$ | $\alpha$ . . | 0·4319 | 1·4353 | 1·4388 | 1·4408 | 1·4457 | 1·4543 | 1·6432 | 1·5221 |
| | $\beta$ . . | 1·4519 | 1·4579 | 1·4618 | 1·4632 | 1·4727 | 1·4778 | 1·4934 | — |
| | $\gamma$ . . | 1·4602 | 1·4635 | 1·4666 | 1·4697 | 1·4844 | 1·4881 | — | 1·5680 |
| $2V$ | . . | 51° 28′ | 53° 32′ | 53° 58′ | 55° 40′ | 57° 16′ | 60° 14′ | 69° 52′ | 75° 28′ |

P. Walden gave for the eq. conductivity, $\lambda$ mho, at 25° with a mol of the salt in $v$ litres:

| $v$ . . | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|
| $\lambda$ . . | 80·6 | 90·6 | 98·9 | 107·2 | 114·3 | 119·9 |

while H. Clausen, and A. Heydweiller obtained for conc. soln., at 18°:

| $v$ . . | 0·203 | 0·405 | 0·81 | 1·62 | 4·05 | 8·1 |
|---|---|---|---|---|---|---|
| $\lambda$ . . | 12·23 | 24·85 | 34·17 | 41·07 | 48·09 | 54·86 |

W. J. Grailich and V. von Lang found the diamagnetism to be strongest in the direction of the (010)-axis. M. Wein studied the electrical conductivity. A. Naumann said that the salt is soluble in acetone. G. N. Wyrouboff prepared the *pentahydrate*, $MgCrO_4.5H_2O$, from the heptahydrate as indicated above; or by crystallizing an aq. soln. above 30°. The yellow crystals are stable, and do not effloresce in air. They are triclinic pinacoids with the axial ratios $a:b:c=0{\cdot}5883:1:0{\cdot}5348$, and $\alpha=82°\ 43'$, $\beta=108°\ 14'$, and $\gamma=103°\ 51'$. They are isomorphous with pentahydrated cupric sulphate. No cleavage was observed. The sp. gr. is 1·954. For the action of heat, *vide supra*.

M. Gröger prepared **ammonium magnesium chromate,** $(NH_4)_2Mg(CrO_4)_2.6H_2O$, from soln. of ammonium chromate and magnesium chloride; and F. J. Malaguti and M. Sarzeau, by adding ammonia to a soln. of magnesium chromate in aq. chromic acid until the hydroxide begins to separate, and then evaporating. The pale yellow crystals were found by A. Murmann to be monoclinic prisms with the axial ratios $a:b:c=0{\cdot}7511:1:0{\cdot}4931$, and $\beta=106°\ 31'$; and M. W. Porter, $0{\cdot}7517:1:0{\cdot}4935$ and $\beta=106°\ 07'$. A. E. H. Tutton and M. W. Porter found the topic axial ratios $\chi:\psi:\omega=6{\cdot}3751:8{\cdot}4811:4{\cdot}1761$. The optic axial angles:

| | red-light | Li· | *C*- | Na- | Tl- | Cd·lines |
|---|---|---|---|---|---|---|
| $2E$ . . | 16° 29′ | 9° 50′ | 14° 29′ | 45° 8′ | 66° 1′ | 77° 43′ |
| $2V$ . . | 10° 47′ | 6° 15′ | 8° 54′ | 26° 53′ | 38° 57′ | 44° 37′ |

They also investigated the effect of temp. on these angles. M. W. Porter found with 0, 43·85, 72·52, and 100 per cent. $(NH_4)_2Mg(CrO_4)_2.6H_2O$, the axial ratios 0·7499 : 1 : 0·4935, and $\beta=106°\ 15'$; 0·7476 : 1 : 0·4928, and $\beta=106°\ 32'$; 0·7451 : 1 : 0·4930, and $\beta=106°\ 55'$; and 0·7409 : 1 : 0·4924, and $\beta=107°\ 6'$ respectively; and the respective refractive indices $\alpha=1·6363, \beta=1·6371, \gamma=1·6531$; $\alpha=1·554$, $\beta=1·557$, $\gamma=1·560$; $\alpha=1·491$, $\beta=1·493$, $\gamma=1·495$; and $\alpha=1·4716$, $\beta=1·4730$, $\gamma=1·4786$. S. Rosch and M. Stürenburg studied the optic axial angles. F. W. Clarke gave 1·84 for the sp. gr. at 16°; and M. W. Porter, 1·835 at about 16°. The mol. vol. is 215·92. C. Schaefer and M. Schubert observed in the ultra-red reflection spectrum a complex maximum at 11·3$\mu$ to 11·42$\mu$; and in polarized light the maximum falls into three groups—11·46$\mu$ parallel to the $a$-axis, 11·28$\mu$ parallel to the $b$-axis, and 10·36$\mu$ parallel to the $c$-axis. A. E. H. Tutton and M. W. Porter found for the indices of refraction :

| | Li- | C- | Na- | Tl- | Cd-light |
|---|---|---|---|---|---|
| $\alpha$ . . | 1·6248 | 1·6265 | 1·6363 | 1·6489 | 1·6571 |
| $\beta$ . . | 1·6250 | 1·6267 | 1·6371 | 1·6509 | 1·6602 |
| $\gamma$ . . | 1·6390 | 1·6411 | 1·6531 | 1·6687 | 1·6799 |

The refractive indices at 80° were about 0·0023 lower than for ordinary temp. The optical properties of isomorphous mixtures of ammonium magnesium sulphate and chromate were examined. F. Rüdorff's diffusion experiments showed that the salt is more or less dissociated in aq. soln. G. Canneri prepared **guanidine magnesium chromate,** $(CH_5N_3)_2.H_2CrO_4.MgCrO_4.6H_2O$, isomorphous with the sulphate. A. Stanley evaporated a soln. obtained by treating a soln. of sodium dichromate with a magnesium salt, and obtained yellow, four-sided prisms and plates of **sodium magnesium chromate,** $Na_2CrO_4.MgCrO_4.3H_2O$. The salt gives off all its water below 200° leaving the reddish-brown, pulverulent anhydride. The *trihydrate* is freely soluble in water and alcohol, but insoluble in ether.

T. Thomson, and E. F. Anthon prepared **potassium magnesium chromate,** $K_2CrO_4.MgCrO_4.2H_2O$, by evaporating a soln. of potassium dichromate mixed with magnesia; M. Gröger, by treating an almost sat. soln. of potassium chromate with a soln. of magnesium chloride. G. N. Wyrouboff said that the *dihydrate* is obtained if the soln. be evaporated over 18°. The triclinic, pinacoidal crystals were found by G. N. Wyrouboff to have the axial ratios $a : b : c=0·6551 : 1 : 0·4326$, and $\alpha=84°\ 35'$, $\beta=102°\ 44'$, and $\gamma=86°\ 38'$. Twinning occurs about the (101)-, $(10\bar{1})$-, and (100)-planes; and the (101)- and $(10\bar{1})$-cleavages are distinct. The optical character is negative. H. G. F. Schröder gave 2·600 for the sp. gr.; E. F. Anthon, 2·59 at 19°; and G. N. Wyrouboff, 2·602 at 16°, and for the mol. vol. 142·5. E. F. Anthon observed that when the salt is heated, it becomes orange-yellow, and melts at dull redness forming a dark red liquid; and E. Schweizer represented the decomposition at a red-heat by $2K_2Mg(CrO_4)_2=2K_2CrO_4+MgO+Mg(CrO_2)_2+3O$. G. Viard said that not $MgO.Cr_2O_3$ but rather $2MgO.Cr_2O_3$ and $5MgO.4Cr_2O_3$ are produced. E. Schweizer said that 100 parts of water dissolve 28·2 parts of the salt at 20°, and 34·3 parts at 60°; and M. Gröger, that the salt is not decomposed by cold water. The salt is insoluble in alcohol. S. H. C. Briggs reported that the *hexahydrate*, $K_2Mg(CrO_4)_2.6H_2O$, is formed by cooling a conc. soln. to —10°. The lemon-yellow crystals can be washed with alcohol and ether. When dried in air at 8°–10°, the salt loses 4 mols. of water. G. N. Wyrouboff said that the hexahydrate is formed by evaporating the soln. below 1·8°. C. von Hauer could not make the hexahydrate. A. Duffour found that the hexahydrate can be obtained if the two chromates are dissolved separately in equimolar proportions in two and a half times their weight of warm water, and the soln. are mixed, filtered, and left to evaporate at a temp. not exceeding 15°. After several days, the hexahydrate separates in tabular crystals, which should be removed at once. The crystals after five or six hours begin to change slowly into the dihydrate. This dehydration is far more rapid at 120° but always stops at the dihydrate. The hexahydrate is thus known only in a metastable state even 10°. The crystals

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are monoclinic and have the axial ratios $a:b:c=0{\cdot}7521:1:0{\cdot}4984$, and $\beta=103°\,54'$. Monoclinic crystals of the hexahydrate, in solid soln. with the hexahydrated potassium magnesium sulphate, can be obtained by the evaporation at 20° of a soln. with 3 mols of the complex sulphate to one mol of the complex chromate. A. Duffour studied the triclinic crystals of solid soln. of hexahydrated potassium magnesium chromate and sulphate.

S. H. C. Briggs prepared **rubidium magnesium chromate,** $Rb_2CrO_4.MgCrO_4.6H_2O$, by a process analogous to that used for the potassium salt. The lemon-yellow crystals are stable in air. T. V. Barker also prepared this salt and found that the axial ratios of the monoclinic crystals are $a:b:c=0{\cdot}7558:1:0{\cdot}4950$, and $\beta=104°\,55'$; M. W. Porter gave $0{\cdot}7540:1:0{\cdot}4960$ and $\beta=104°\,52'$. A. E. H. Tutton and M. W. Porter gave for the optic axial angle:

| | Li- | C- | Na- | Tl- | Cd-light |
|---|---|---|---|---|---|
| $2V$ . . | 88° 27′ | 88° 4′ | 86° 33′ | 84° 31′ | 83° 15′ |

They also gave for the topic axial ratios $\chi:\psi:\omega=6{\cdot}3403:8{\cdot}4246:4{\cdot}1727$; and the sp. gr. 2·466 at 20°/4°. M. W. Porter gave 2·463 at about 16°, and the mol. vol. at 20° is 215·48; F. A. Henglein gave 217·0. M. W. Porter found that the indices of refraction are $\alpha=1{\cdot}6363$, $\beta=1{\cdot}6371$, and $\gamma=1{\cdot}6528$. A. E. H. Tutton and M. W. Porter found for the indices of refraction:

| | Li- | C- | Na- | Tl- | Cd-light |
|---|---|---|---|---|---|
| $\alpha$ . . | 1·6105 | 1·6118 | 1·6217 | 1·6342 | 1·6426 |
| $\beta$ . . | 1·6208 | 1·6221 | 1·6330 | 1·6466 | 1·6561 |
| $\gamma$ . . | 1·6310 | 1·6326 | 1·6435 | 1·6517 | 1·6672 |

The refractive indices, $\alpha$, $\beta$, and $\gamma$, diminish respectively by 0·0019, 0·0024, and 0·0025 on raising the temp. to 80°. M. W. Porter examined the optical properties of isomorphous mixtures of ammonium and rubidium magnesium chromates. M. W. Porter showed that the ammonium and rubidium magnesium chromates are completely isomorphous. Selecting some of the observed data for the isomorphous mixtures containing 0, 35·35, 74·05, and 100 per cent. of the ammonium salt, the axial ratios were $0{\cdot}7540:1:0{\cdot}4960$, and $\beta=104°\,52'$; $0{\cdot}7526:1:0{\cdot}4928$, and $\beta=105°\,23'$; $0{\cdot}7522:1:0{\cdot}4931$, and $\beta=105°\,47'$; and $0{\cdot}7517:1:0{\cdot}4935$, and $\beta=106°\,9'$ respectively; the sp. gr., 2·463, 2·211, 1·998, and 1·835 respectively; and the indices of refraction $\alpha=1{\cdot}6216$, $\beta=1{\cdot}6330$, and $\gamma=1{\cdot}6439$; $\alpha=1{\cdot}6268$, $\beta=1{\cdot}6371$, and $\gamma=1{\cdot}6468$; $\alpha=1{\cdot}6330$, $\beta=1{\cdot}6368$, and $\gamma=1{\cdot}6493$; and $\alpha=1{\cdot}6363$, $\beta=1{\cdot}6371$, and $\gamma=1{\cdot}6538$ respectively. S. H. C. Briggs prepared **cæsium magnesium chromate,** $Cs_2Mg(CrO_4)_2.6H_2O$, by the method employed for the potassium salt. The cæsium salt is rather more stable than the rubidium salt. T. V. Barker gave for the axial ratios of the monoclinic crystals $a:b:c=0{\cdot}7420:1:0{\cdot}4886$, and $\beta=106°\,7'$. A. E. H. Tutton and M. W. Porter gave for the optic axial angles:

| | Li- | C- | Na- | Tl- | Cd-light |
|---|---|---|---|---|---|
| $2E$ . . | 131° 3′ | 131° 27′ | 132° 55′ | 133° 22′ | — |
| $2Va$ . . | 67° 9′ | 67° 7′ | 67° 3′ | 66° 33′ | 65° 57′ |

The topic axial ratios are $\chi:\psi:\omega=6{\cdot}4441:8{\cdot}6718:4{\cdot}2388$; the sp. gr. is 2·747 at 20°/4°; and the mol. vol. 227·62; F. A. Henglein gave 229·2. A. E. H. Tutton and M. W. Porter found the indices of refraction to be:

| | Li- | C- | Na- | Tl- | Cd-light |
|---|---|---|---|---|---|
| $\alpha$ . . | 1·6257 | 1·6271 | 1·6369 | 1·6493 | 1·6578 |
| $\beta$ . . | 1·6310 | 1·6324 | 1·6425 | 1·6552 | 1·6640 |
| $\gamma$ . . | 1·6424 | 1·6438 | 1·6547 | 1·6683 | 1·6778 |

A rise of temp. to 80° results in the reduction of the indices by about 0·0026.

Normal **zinc chromate,** $ZnCrO_4$, is not easy to prepare, for, if a large proportion of water be present, a basic salt is formed; and if very conc. soln. are employed at a high temp., oxygen may be evolved. J. Milbauer[15] said that there is a 72 per cent. conversion to chromate when a mixture of chromic oxide and zinc oxide or

carbonate is heated to 480° in oxygen at 12 atm. press. S. H. C. Briggs did not succeed in preparing the normal chromate in a non-aqueous solvent. J. Schulze obtained normal zinc chromate by heating the dichromate with zinc hydroxide in a sealed tube to 200°; and S. H. C. Briggs recommended heating for 3 hrs. at 220° in a sealed tube a mixture of 4·5 grms. $CrO_3$, 4·5 grms. zinc carbonate with 70 per cent. ZnO, and 5 c.c. of water. According to M. Gröger, by shaking zinc oxide with a soln. of chromic acid, in different proportions, and after a few days, determining the compositions of the filtrate, and precipitate, the composition of the soln. is found to vary continuously, Fig. 49, but the composition of the solid phase shows discontinuities, Fig. 49; if the concentrations of the soln. be expressed in mols per litre, the solid phases correspond with

| | | | | | |
|---|---|---|---|---|---|
| CrO . . | 0·00010 | 0·1140 | 0·6660 | 1·92 | 4·62 |
| $ZnO_3$ . | 0·00016 | 0·0720 | 0·3720 | 1·03 | 2·41 |
| Solid. | $4ZnO.CrO_3.3H_2O$ | $3ZnO.CrO_3.2H_2O$ | $2ZnO.CrO_3.1\frac{1}{2}H_2O$ | | $3ZnO.2CrO_3$ |

Beyond the limit $CrO_3 : ZnO = 4·62 : 2·41$, the solid phase is the *monohydrate*, $ZnCrO_4.H_2O$. The soln. also contained some zinc mono- and di-chromates. All the solids were crystalline excepting the 3 : 2 : 1 compound. The monohydrated monochromate did not lose water at 125°; and it was not found possible to convert it into the insoluble, anhydrous salt.

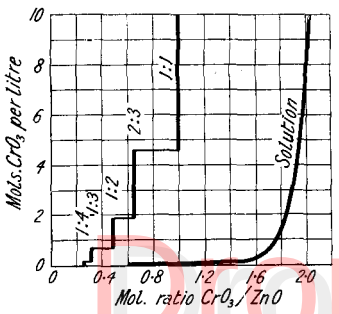



FIG. 49.—Equilibrium Conditions in the System: $ZnO$–$CrO_3$–$H_2O$ at 25°.

According to J. Schulze, normal zinc chromate furnishes microscopic, lemon-yellow, prismatic crystals, which are insoluble in water, easily soluble in acids, and are decomposed by boiling with water to form soluble dichromate and an insoluble basic chromate. M. Gröger's observations on the action of water on the monohydrate are summarized in Fig. 49. H. S. Taylor and G. I. Lavin studied the action of activated hydrogen on the chromate. E. C. Franklin said that zinc chromate is insoluble in liquid ammonia; and A. Naumann, that it is insoluble in acetone. M. Gröger said that the product of the action of zinc chloride on an excess of ammonium chromate is probably **zinc amminochromate,** $ZnCrO_4.NH_3.H_2O$. This *monohydrate* is decomposed by water; and forms zinc chromate when heated giving off nitrogen and water. L. Bieler prepared the *trihydrate* of **zinc tetramminochromate,** $ZnCrO_4.4NH_3.3H_2O$, by dissolving the basic salt in the smallest amount of aq. ammonia, and adding to the filtrate 2 or 3 times its vol. of absolute alcohol. The crystals are then dissolved in aq. ammonia, some ammonium chloride is added, and the salt again precipitated with alcohol. The rhombic plates rapidly effloresce forming a yellow powder. The salt is freely soluble in aq. ammonia, and in dil. acids; but it is decomposed by water with the separation of a basic salt. F. J. Malaguti and M. Sarzeau obtained the *pentahydrate*, $ZnCrO_4.4NH_3.5H_2O$, by allowing a basic salt to stand for 12 hrs. in a closed flask with sat. aq. ammonia. The salt is precipitated from the clear soln. by adding alcohol. The yellow cubes are decomposed by water; they are soluble in aq. ammonia; and insoluble in alcohol and ether. By mixing the 4 : 1 : 5 basic chromate with an excess of aq. ammonia, and adding alcohol, F. J. Malaguti and M. Sarzeau obtained yellow masses of acicular crystals of **zinc decamminochromate,** $2ZnO.3CrO_3.10NH_3.10H_2O$.

A number of basic salts has been reported; and a number of these, of indefinite composition, forms the so-called *zinc yellow*, *zinc chrome*, *Zinkgelb*, *jaune de zinc*, or *yellow ultramarine* which is employed as a pigment. T. Thomson prepared the colour in 1825; and W. A. Lampadius, in 1829. C. O. Weber prepared a bright yellow, flocculent powder by treating a soln. of zinc sulphate and sodium carbonate

with potassium chromate. Its composition approximated $4ZnO.3CrO_3.nH_2O$. M. Prud'homme and F. Binder obtained a basic salt by heating zinc hydroxide with a soln. of potassium chromate and dichromate. The zinc yellows have been discussed by L. Bock, J. G. Gentele, G. Zerr and G. Rübencamp, F. Rose, S. Tschelnitz, etc. The colour was discussed by W. Ackroyd. The conditions of equilibrium of the basic salts are indicated in Fig. 49. M. Gröger, and B. Skormin obtained **zinc trioxychromate,** $4ZnO.CrO_3.3H_2O$, as a *trihydrate*, by mixing soln. of zinc chloride and sodium chromate at ordinary temp.; by treating the basic potassium or ammonium zinc chromates with hot water; and by the action of chromic acid on zinc oxide in accord with the conditions indicated in Fig. 49. J. Prüssen and H. Philippona obtained it by boiling the precipitate obtained by mixing zinc sulphate and potassium chromate soln. with much water for a long time. F. J. Malaguti and M. Sarzeau said that the *pentahydrate* is formed when zinc carbonate is treated with a soln. of chromic acid. H. Kopp added that if the chromic acid contains sulphuric acid as impurity, the precipitate will be contaminated with basic zinc sulphate. M. Gröger obtained **zinc dioxychromate,** $3ZnO.CrO_3.2H_2O$, by the action of chromic acid on zinc oxide in accord with the conditions indicated in Fig. 49. M. Gröger, and B. Skormin likewise prepared **zinc oxychromate,** $2ZnO.CrO_3.1\frac{1}{2}H_2O$. The *hemitrihydrate* was also prepared by T. Thomson, A. Bensch, and J. Prüssen and H. Philippona by the action of a soln. of zinc sulphate on one of potassium chromate. L. Vanino and F. Ziegler added a sat. soln. of chromic acid to a mol. eq. of zinc oxide suspended in water, constantly agitated. The zinc oxide passed into soln. with a rise of temp. After a time an orange or brownish-yellow product separated approximating $ZnO.ZnCrO_4.nH_2O$. S. H. C. Briggs obtained the *monohydrate* as a yellow, crystalline powder by heating for 3 hrs. in a sealed tube a mixture of 4 grms. chromium trioxide, 3 grms. of zinc oxide, and 20 grms. of water. M. Gröger also prepared **zinc oxybischromate,** $3ZnO.2CrO_3.H_2O$, by the action of chromic acid on zinc oxide in accord with the conditions indicated in Fig. 49.

It is doubtful if the **potassium zinc chromates** or the **ammonium zinc chromates** have been prepared. The products which have been reported may be adsorption products of the basic salts. M. Gröger reported products with the mol. ratios $K_2O : ZnO : CrO_3 : H_2O = 1 : 5 : 4 : 6$; $1 : 4 : 4 : 3$; and $1 : 1 : 2 : 2$. L. Vanino and F. Ziegler found that on mixing a sat. soln. of potassium dichromate at 100° with zinc sulphate soln. sat. at 39°, so that the ratio $CrO_3 : ZnO$ is 1 : 1, or by pouring one soln. into the other, in either case, a deep yellow precipitate is formed; which after filtering and washing approximates **potassium zinc trioxybischromate,** $2K_2O.3ZnO.2ZnCrO_4$. It is supposed that the zinc chromate first formed hydrolyzes when washed with water, forming this basic chromate or a mixture of basic chromates. He showed that the action of an excess of zinc chloride in an aq. soln. of *N*- or $3N\text{-}K_2CrO_4$ leads to the formation of a yellow, granular precipitate, which has the composition $4ZnO.K_2O.4CrO_3.3H_2O$. By repeated treatment with hot water, this is converted into the insoluble basic zinc chromate, $ZnCrO_4.3Zn(OH)_2$, which is a dark yellow powder. When fused, the zinc potassium chromate evolves oxygen, the residue consisting of potassium chromate and insoluble violet zinc chromite, $8ZnO.3Cr_2O_3$. The proportion of potassium, and, to a less extent, that of chromium, is increased by the use of an excess of the potassium chromate; with *N*-soln., the precipitate has the mol. composition $ZnO.0{\cdot}394K_2O.1{\cdot}094CrO_3$; with $3N$-soln., $ZnO.0{\cdot}486K_2O.1{\cdot}222CrO_3$. When treated with hot water, these precipitates yield the foregoing basic zinc chromate. These precipitates are of a deeper yellow than that formed in presence of excess of zinc salt, but after prolonged contact (2 weeks) with the mother-liquor they assume the colour and composition of the latter. The action of zinc chloride on sodium chromate leads to the formation of basic zinc chromate, $ZnCrO_4.3Zn(OH)_2$, which is obtained as a horny mass. Ammonium chromate and excess of zinc chloride give rise to a dark yellow, granular precipitate, $ZnO.0{\cdot}279(NH_4)_2O.0{\cdot}822CrO_3$, which is possibly a mixture, and is

decomposed by cold water. The orange-yellow precipitate, formed by the action of an excess of ammonium chromate on zinc chloride, is stable to water or its mother-liquor and has the composition $(NH_4)_2CrO_4.ZnCrO_4.Zn(OH)_2$. When strongly heated, it decomposes suddenly, evolving nitrogen and water vapour; the residue is a powder consisting of zinc oxide and chromite, $2ZnO.Cr_2O_3$. These salts were discussed by J. J. Berzelius, C. Freese, J. Prüssen and H. Philippona, C. O. Weber, B. Skormin, and L. Bock. According to S. H. C. Briggs, **ammonium zinc diamminobischromate,** $(NH_4)_2.Zn(CrO_4)_2.2NH_3$, is formed in lemon-yellow crystals by adding an excess of ammonium chloride or nitrate to a soln. of 10 grms. of zinc hydroxide in 20 grms. of chromium trioxide in a little water and all diluted to 200 c.c. M. Gröger obtained it in prismatic crystals by the action of ammonium chromate on zinc chloride in the presence of a large excess of ammonia. M. Gröger also reported **ammonium zinc triamminosexichromate,** $(NH_4)_4Zn_4(CrO_4)_6.3NH_3$, in orange-yellow crystals, by dropping 10 c.c. of $2M$-$ZnCl_2$ into 50 c.c. of a cold, sat. soln. of ammonium chromate.

J. Schulze prepared normal **cadmium chromate,** $CdCrO_4$, by heating in a sealed tube at 200°, a mixture of cadmium dichromate and cadmium hydroxide. The pale orange-coloured powder is insoluble in water, and soluble in acids. It gradually decomposes when boiled with water. S. H. C. Briggs obtained it by heating a mixture of 3·5 grms. cadmium oxide, 3·6 grms. chromium trioxide, and 20 c.c. of water in a sealed tube at 200° for 3 hrs. He said that the yellow powder consisting of prismatic crystals is insoluble in a hot, conc. soln. of cadmium sulphate. G. Viard said that the salt is very stable and begins to decompose at dull redness. When the filtrate is allowed to stand for some time, it deposits crystals of the *dihydrate*, $CdCrO_4.2H_2O$. F. J. Malaguti and M. Sarzeau prepared **cadmium tetramminochromate,** $CdCrO_4.4NH_3.3H_2O$, by the method employed for the corresponding zinc salt. By adding alcohol to the acidic soln. of the oxychromate, they obtained a crystalline precipitate of **cadmium pentamminochromate,** $2CdO.3CrO_3.5NH_3.8H_2O$. According to M. Gröger, the ammonium salt, $(NH_4)_2O.4CdO.4CrO_3.3H_2O$, can be regarded as **cadmium hemiamminochromate,** $2CdCrO_4.NH_3.2H_2O$; and when the salt $2(NH_4)_2CrO_4.2CdCrO_4.NH_3.3H_2O$ is allowed to stand in its mother-liquor, for 3 weeks, **cadmium amminochromate,** $CdCrO_4.NH_3.H_2O$, is formed.

F. J. Malaguti and M. Sarzeau prepared **cadmium trioxybischromate,** $3CdO.2CdCrO_4.8H_2O$, by treating a soln. of a cadmium salt with potassium chromate, and boiling the precipitate with oft-removed water until the colour no longer changes. The orange-yellow powder is very slightly soluble in water. C. Freese reported **cadmium oxychromate,** $CdO.CdCrO_4.H_2O$, to be formed from boiling soln. of cadmium sulphate and potassium chromate. Only when a large excess of chromate is present is the product free from acid. C. Freese suggested that the trioxybischromate is really this salt; while B. Skormin obtained a product $4CdO.3CdCrO_4$ with 4·5 to 6·0$H_2O$. The nature of the product, said M. Gröger, depends on the time of contact of the precipitate with boiling water. Consequently the nature of the basic salts of cadmium chromate is still *sub judice*. B. Skormin described cadmium tetroxytrischromate, $4CdO.3CdCrO_4.nH_2O$. According to F. Rose, the basic chromate has been used as a yellow pigment; but its cost limits it to fine art work.•

According to M. Gröger, cadmium chloride and ammonium chromate in aq. soln. interact to form a dark yellow precipitate consisting of microscopic prisms of **ammonium cadmium dihydroxyquadrichromate,** $(NH_4)_2CrO_4.3CdCrO_4.Cd(OH)_2.2H_2O$. The action of hot water on this precipitate is to convert it into a basic cadmium chromate; and when heated, the salt leaves a green residue—possibly cadmium chromite. If 10 c.c. of a soln. of cadmium chloride be dropped into 50 c.c. of a soln. of ammonium chromate, with constant stirring, deep yellow, microscopic prisms are precipitated. The composition corresponds with **ammonium cadmiumamminoquadrichromate,** $2(NH_4)_2CrO_4.2CdCrO_4.NH_3.3H_2O$. S. H. C. Briggs obtained **ammonium cadmium diamminochromate,** $(NH_4)_2CrO_4.CdCrO_4.2NH_3$, by

dissolving 26 grms. of chromium trioxide and 13 grms. of cadmium oxide in a little water, diluting the soln. to 200 c.c. and adding ammonia so long as the soln. remained clear. The filtrate is allowed to stand for 2 or 3 days. The yellow crystals decompose suddenly when heated to 280°–290°. The **potassium cadmium chromates** resemble the corresponding zinc salts. M. Gröger reported products with the mol. ratios $K_2O : CdO : CrO_3 : H_2O = 1 : 7 : 5 : 3$; $1 : 4 : 4 : 3$; $1 : 3 : 2 : 3$; $1 : 1 : 2 : 2$; and $1 : 1 : 4 : 2$. G. Krüss and O. Unger also prepared the $1 : 1 : 4 : 2$ complex; and B. Skormin, $1 : 7 : 5 : 3$. M. Gröger observed that on mixing aq. soln. of potassium chromate and pure cadmium chloride, a canary-yellow, granular precipitate is formed having the composition $K_2CrO_4.3CdCrO_4.Cd(OH)_2.2H_2O$. Contrary to K. Preis and B. Rayman's statement, this same precipitate is formed by the action of cadmium sulphate and potassium chromate. Cadmium potassium chromate is more stable to boiling water than is zinc potassium chromate; but is finally converted into a lemon-yellow powder, 84·53 per cent. of which is cadmium chromate. On mixing aq. soln. of cadmium chloride and sodium chromate, a yellow, flocculent precipitate is formed which rapidly becomes granular; it is a basic cadmium chromate which easily loses chromic acid when washed with water and absorbs carbon dioxide when exposed to air. When equal vols. of cadmium chloride and sodium chromate soln. are mixed hot and boiled for three days, during which period the precipitate formed is washed twenty-four times, the residue obtained has the mol. proportions $CdO : 0{\cdot}342CrO_3 : 1{\cdot}428H_2O$.

The early workers—L. N. Vauquelin,[16] C. M. Marx, S. M. Godon de St. Menin, etc.—prepared a basic mercurous chromate by treating a soln. of mercurous nitrate with potassium chromate. The presence of nitrous acid prevents the precipitation by reducing chromic acid to chromic oxide. If an excess of nitric acid be present, part of the chromic acid forms mercuric oxide and chromic nitrate and the liquid becomes amethyst-blue, but, on adding more mercurous nitrate, the whole of the chromium is precipitated as mercurous chromate. The same product is obtained whether the soln. be hot or cold, and, added P. and M. M. Richter, statements to the contrary are based on the use of mercurous nitrate contaminated with nitrite. The analyses of L. Gmelin, F. Fichter and G. Oesterheld, and S. M. Godon de St. Menin agree with the assumption that the basic salt—**mercurous oxytrischromate,** $Hg_2O.3Hg_2CrO_4$—is formed. C. Freese, and F. Fichter and G. Oesterheld also obtained it by the hydrolysis of mercurous chromate. The bright red powder turns black when exposed to light; and at a red-heat it is decomposed into chromic oxide, oxygen, and mercury. H. Rose said that it dissolves very sparingly in cold water, but freely in boiling water to form a mercuric salt. A. A. Hayes said that hydrochloric acid converts it into mercurous chloride and chromic acid; ammonia converts it into a black powder which, together with the mercurous oxide, contains about half the chromium as chromic oxide. R. H. Brett said that it is slightly soluble in aq. soln. of ammonium chloride or nitrate. A. A. Hayes added that it is slightly soluble in nitric acid. S. Darby found that basic mercurous chromate is transformed into normal **mercurous chromate,** $Hg_2CrO_4$, by boiling it with nitric acid; and F. Fichter and G. Oesterheld obtained it by dissolving basic mercurous chromate in boiling $5N\text{-}HNO_3$, and cooling; and also by treating a normal soln. of mercurous nitrate with potassium chromate. C. Freese treated an excess of a soln. of mercurous nitrate with potassium dichromate, and washed the product with dil. nitric acid; L. Schulerud added that if twice the proportion of mercurous nitrate be not present, some dichromate is formed. S. Darby found that a complex salt is produced when equimolar parts of potassium dichromate and mercury cyanide are mixed in soln. and enough nitric acid added to the boiling soln. to dissolve the precipitate; on cooling, mercurous chromate is deposited as a crystalline powder. J. A. Atanasiu found that in the electrometric titration of soln. of mercurous nitrate and potassium chromate there is a break corresponding with the formation of mercurous dichromate. Mercurous chromate may form red, rhombic plates, or it may appear as a brown, amorphous precipitate which soon

becomes red, and crystalline. F. Fichter and G. Oesterheld said that it should be precipitated from ice-cold soln. since hydrolysis occurs at higher temp., and basic salts are formed. O. D. Swett said that nitric acid is a good solvent for this chromate. According to S. Darby, hydrochloric acid precipitates mercury quantitatively from the soln. of the salt in nitric acid; and ammonia, or potassium hydroxide gives black precipitates. P. and M. M. Richter found that potassium bromide, iodide, and cyanide react similarly; the iodide, for example, precipitates green mercurous iodide which, with more potassium iodide, forms mercury and mercuric iodide, and thus dissolves as $KHgI_3$; with potassium cyanide, the complex $2K_2CrO_4.3HgCy_2$ is formed. F. Fichter and G. Oesterheld said that the salt is less soluble in a soln. of potassium chromate than it is in water. A. Naumann found that the salt is insoluble in acetone; and H. Rose, that it is slightly soluble in dil. nitric acid, very soluble in conc. nitric acid, soluble in a soln. of potassium cyanide, and insoluble in a soln. of mercurous nitrate.

F. Fichter and G. Oesterheld observed that the hydrolysis of normal mercurous chromate furnishes the oxytrischromate (*q.v.*), and subsequently **mercurous oxybischromate,** $Hg_2O.2Hg_2CrO_4$. This salt is formed when freshly precipitated mercurous chromate is boiled with water so long as chromic acid passes into soln. If precipitated mercurous chromate be allowed to stand under the mother-liquid, containing an excess of mercurous nitrate for 7 days, or if it be boiled with mother-liquid for 4 hrs., dark red microscopic needles of the oxybischromate are formed. P. and M. M. Richter obtained **mercurous dioxychromate,** $2Hg_2O.Hg_2CrO_4$, by the action of alkalies on mercurous chromate. This salt forms black crystals, which when dried at a high enough temp. becomes dark green or brownish-black owing to the loss of a little mercury—*vide infra*, oxydimercuriammonium chromate; for the properties of these basic chromates, *vide supra*, mercurous oxytrichromate.

M. Gröger reported **potassium mercurous chromate,** $K_2CrO_4.Hg_2CrO_4$, to be formed by the action of a soln. of mercurous nitrate, containing as little free nitric acid as possible, on a sat. soln. of potassium chromate. After shaking for a couple of weeks, the solid is separated by a suction filter, and dried on a porous tile. The brownish-yellow product decomposes when melted; and when treated with water it furnishes basic mercurous chromate.

According to A. Geuther, and A. J. Cox, if equimolar parts of chromium trioxide and yellow mercuric oxide be boiled with water, red crystals of **mercuric chromate,** $HgCrO_4$, are formed. The dark garnet-red, rhombic prisms become still darker when heated, but they lose no weight at 135°; at a red-heat, the salt decomposes yielding mercury, oxygen, and chromic oxide. The salt is hydrolyzed by cold water, and with hot water, a residue $7HgO.2CrO_3$ is formed; the hydrolysis can proceed further until finally mercuric oxide remains. If the conc. of the chromic acid be less than 0·46 mol $CrO_3$ per litre, the normal chromate is unstable—Fig. 50. Cold conc. nitric acid transforms the salt into $7HgO.2CrO_3$; moderately conc. nitric and sulphuric acids also form $7HgO.2CrO_3$. The salt is completely soluble in hydrochloric acid, and from this soln., alkali-lye precipitates mercuric oxide. M. Gröger obtained **mercuric diamminochromate,** $HgCrO_4.2NH_3.H_2O$, by dropping a soln. of 8·64 grms. of mercuric oxide in 6 c.c. of nitric acid of sp. gr. 1·41, and diluted to 20 c.c. into 50 c.c. of a soln. of 2 mols. of ammonium chromate. A. Naumann said that the mercuric chromate is insoluble in ethyl acetate and in acetone.

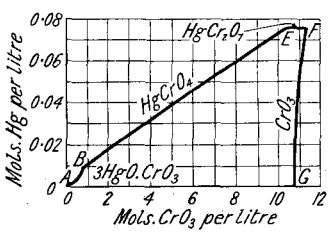



FIG. 50.—Conditions of Equilibrium of Mercuric Chromates at 25°.

A. J. Cox studied the ternary system: $HgO$–$CrO_3$–$H_2O$ at 25°, and found that under these conditions only one basic salt is formed. The invariant points, *A*, *B*, *E*, *F*, *G*, Fig. 50, are indicated in Table IV. where concentrations are expressed

TABLE IV.—INVARIANT POINTS IN THE SYSTEM $HgO$–$CrO_3$–$H_2O$ AT 25°.

| Mols $CrO_3$. | Mols Hg. | Solid phases. | Fig. |
|---|---|---|---|
| — | — | $HgO + 3HgO.CrO_3$ | *A* |
| 0·456 | 0·035 | $3HgO.CrO_3 + HgCrO_4$ | *B* |
| 10·46 | 0·758 | $HgCrO_4 + Hg_2Cr_2O_7$ | *E* |
| 11·11 | — | $Hg_2Cr_2O_7 + CrO_3$ | *F* |
| 10·8 | — | $CrO_3$ | *G* |

in mols per litre. The results are also shown graphically in Fig. 50. It was also found that at 50°

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $CrO_3$ | 0·00013 | 0·0047 | 0·705 | 0·499 | 0·620 | 0·740 | 1·006 |
| Hg | small | 0·00015 | 0·0745 | 0·049 | 0·066 | 0·072 | 0·1 |
| | $HgO$ | $3HgO.CrO_3$ | | labile | | stable | |
| | | | | $HgCrO_4$ | | | |

N. A. E. Millon boiled yellow mercuric oxide with a soln. of potassium dichromate and obtained **mercuric dioxychromate,** $2HgO.HgCrO_4$, or $3HgO.CrO_3$. B. Skormin obtained the same product from freshly precipitated yellow mercuric oxide and an excess of a soln. of potassium dichromate. N. A. E. Millon, B. Skormin, C. Freese, and A. J. Cox also obtained it by treating a soln. of mercuric nitrate with potassium dichromate or chromate. The conditions of equilibrium are illustrated by Fig. 51. N. A. E. Millon found that the same product is obtained with mercuric chloride, but A. Caillot could not prepare it with mercuric bromide. A. J. Cox, and A. Geuther obtained it by the hydrolysis of mercuric chromate; and A. Geuther, by pouring a cold solution of mercuric carbonate in conc. nitric acid into cold water—the precipitate is at first yellow, but soon becomes scarlet-red. B. Skormin also prepared this salt. A. J. Cox showed that the minimum conc. of acid in which the salt is stable is $0{\cdot}00026N$-$HNO_3$ at 50°. J. L. Gay Lussac and L. J. Thénard found that mercuric chromate is decomposed with incandescence when heated with potassium.

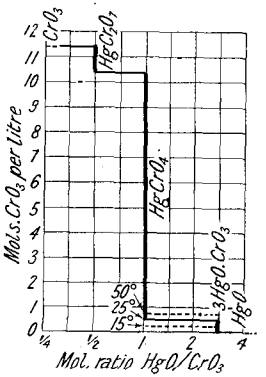



FIG. 51. — Conditions of Equilibrium in the System: $HgO$–$CrO_3$–$H_2O$ at 25°.

Several other basic salts have been reported; thus, E. Jäger and G. Krüss, and F. W. Clarke and D. Stern reported $6HgO.CrO_3$, but neither B. Skormin, nor A. J. Cox could verify its existence; E. Jäger and G. Krüss also reported $5HgO.CrO_3$, but A. J. Cox could not confirm the result; N. A. E. Millon, and F. W. Clarke and D. Stern, $4HgO.CrO_3$, but neither A. J. Cox, nor B. Skormin could accept the evidence; M. Gröger stated that this compound forms the ammino compound $3(4HgO.CrO_3).2NH_3.3H_2O$, by extraction with a soln. of ammonium chromate. A. Geuther, and F. W. Clarke and D. Stern reported $7HgO.2CrO_3$, but C. Freese, B. Skormin, and A. J. Cox were unable to verify the result; and A. Geuther reported $2HgO.CrO_3$, but A. J. Cox could not confirm the result. F. Rose mentioned the use of the basic chromates as pigments—*purple red*, or *chrome red*.

F. M. Litterscheid added ammonia to a soln. of potassium dichromate, mixed with an excess of mercuric chloride, in the cold until the liquid had an alkaline reaction; and obtained **dimercuriammonium chromate,** $(NHg_2)_2CrO_4.2H_2O$. The same product was obtained by adding an excess of ammonia to a cold soln. of mercuric chloride, and then adding a soln. of potassium chromate or dichromate. The lemon-yellow precipitate gave off no water when heated for many hours at 100°; it is virtually insoluble in water, and in a cold 10 per cent. soln. of ammonia —free from ammonium salts. The moist salt dissolves in soln. of ammonium salts.

The moist compound is freely soluble in 10 per cent. hydrochloric acid, but if the salt has been dried it dissolves with difficulty. The dried salt is easily soluble in 25 per cent. hydrochloric acid; and is insoluble in boiling, conc. nitric or sulphuric acid, with gradual decomposition; the moist salt is more easily attacked by these acids. F. W. Clarke and D. Stern obtained what they regarded as a complex salt, *ammonium dimercuriammonium chromate*. According to E. C. Franklin, a salt of this composition can be regarded as *mercuric hydroxyimidochromate*, $(HO.Hg.NH.Hg)_2CrO_4$; or as *oxydimercuriammonium chromate*, $(NH_2.Hg.O.Hg)_2CrO_4$. F. Fichter and G. Oesterheld obtained it by the action of aq. ammonia on mercurous chromate, and said that P. and M. M. Richter were wrong in saying that the product of the action is mercurous dioxychromate; the action of alkalies furnishes a mixture of mercurous oxide, or mercuric oxide and mercury. C. Hensgen obtained this product by the action of a hot, conc. soln. of ammonium chromate on mercuric chloride, and by boiling the complex dichromate with aq. ammonia or potash-lye; C. H. Hirzel, by digesting basic oxydimercuriammonium chromate (*vide infra*) with aq. ammonia, and washing with hot water; and B. Skormin, by mixing an excess of a cold, conc. soln. of ammonium chromate with mercuric nitrate, and boiling the orange-yellow, amorphous precipitate with water until it gives no reaction for nitric acid, and is colourless. The yellow product can be represented as an amidochromate, $3HgO.Hg(NH_2)_2CrO_3$; it becomes greyish-yellow at 100°, and begins to decompose into ammonia and a basic *mercuric amidochromate*, $3HgO.Hg(NH_2)_2CrO_3$. When heated in a tube, it gives a yellowish-red sublimate and mercury; it glows brightly with sparking when heated in air; it is not decomposed by potash-lye, but with a boiled soln. ammonia is evolved; it develops ammonia when heated with a soln. of potassium iodide; and it is soluble in hydrochloric acid, but nitric and sulphuric acids have scarcely any action.

C. H. Hirzel prepared **oxydimercuriammonium mercuric oxyquadrichromate,** $HgO.3HgCrO_4(NH_2.Hg.O.Hg)_2CrO_4$. He said that a cold soln. of ammonium dichromate has no apparent action on yellow mercuric oxide; but when the mixture is boiled this salt is formed as an orange-yellow, sandy powder. C. Hensgen regarded it as a mixture of mercuric oxide or basic mercuric chromate, and ammonium oxydimercuriammonium dichromate; and E. C. Franklin represented it by the formula $3HgCrO_4.HgO.(HO.Hg.NH.Hg)_2CrO_4$. C. H. Hirzel found that when heated in a tube, the compound darkens in colour and then decomposes with a feeble detonation; or it may yield nitrous vapours, a yellow sublimate of mercury, and chromic oxide. Ammonia transforms it into lemon-yellow oxydimercuriammonium chromate; potash-lye makes the colour paler, but gives no ammonia; boiling soln. of potassium iodide or sulphide liberate the nitrogen quantitatively as ammonia; conc. nitric acid decomposes it without its passing into soln.; and it forms a reddish-yellow soln. with hydrochloric acid.

S. Löwenthal described *mercuric amidochromate*, $Hg_3NH_2(CrO_4)_2$; and M. Gröger said that *potassium mercuric chromate* is not produced by treating mercuric nitrate or chloride as in the analogous process for the mercurous salt, but rather yields a basic chromate which adsorbs potassium chromate.

A. J. Fairrie,[17] and C. W. Eliot and F. H. Storer treated a soln. of potash-alum with potassium chromate, and obtained a precipitate which after pressing, corresponded with **aluminium dioxychromate,** $Al_2O_2.CrO_4.nH_2O$. M. Siewert, and A. Maus also dissolved aluminium hydroxide in a soln. of chromic acid, and on evaporating the liquid, obtained aluminium hydroxide, and an acidic soln. E. Fleischer observed that no precipitate is produced by adding potassium dichromate to a soln. of potash-alum; and when the liquid is evaporated alum first crystallizes out, and then potassium dichromate. There is here no satisfactory evidence of the formation of an aluminium chromate. L. Blanc, however, regarded the formation of the basic chromate as proved. According to M. Gröger, the addition of aq. potassium chromate to a soln. of potassium-alum precipitates basic

aluminium sulphates ; as the quantity of the chromate is increased, the precipitate becomes mixed with an increasing amount of chromate ; when the alum and potassium chromate are in the ratio $Al_2O_3 : 2CrO_3$, no precipitate is formed. On mixing soln. of aluminium chloride and potassium chromate, a yellow precipitate is formed which has the composition $2Al_2O_3.CrO_3.6H_2O$ ; the precipitation of the aluminium is not complete until 3 mols of potassium chromate have been added for each mol of aluminium chloride. Soln. made by dissolving aluminium hydroxide in chromic acid always contain $Al_2O_3$ and $CrO_3$ in the proportion of 1 : 1·4 to 1·45 ; from this soln., the insoluble basic chromate mentioned above separates on keeping. No indication was observed of the formation of the compound $Al_2O_3.CrO_3.7H_2O$, described by A. J. Fairrie. N. A. Orloff said that aluminium chromate, like beryllium chromate, is hydrolyzed by water without forming any definite basic salt; and L. Petrik represented the reaction: $Al_2(SO_4)_3+3K_2CrO_4+3H_2O = Al_2(OH)_6+3CrO_3+3H_2SO_4$—*vide supra*, the colour of chromic oxide. S. H. C. Briggs added a soln. of 4 grms. of hydrated aluminium chloride in 25 c.c. of water to a soln. of 15 grms. of sodium chromate in 30 c.c. of water, and heated the mixture for an hour on the water-bath. The filtered precipitate was washed with a little water, and dried in vacuo. A mixture of 2 grms. of chromic trioxide, 2 c.c. of water, and 1·8 grms. of the powdered product was heated in a sealed tube at 200° to 210° for 4 hrs., and the crystalline, insoluble, lemon-yellow product corresponded with **aluminium oxydichromate,** $3Al_2O_3.2CrO_3.6H_2O$, or $Al_2O_3.2(AlO)_2CrO_4.6H_2O$.

According to R. E. Meyer,[18] and C. Winkler, a soln. of a neutral salt of indium gives an insoluble precipitate of an **indium chromate** when treated with an alkali chromate. A soln. of indium sesquioxide in aq. chromic acid, does not crystallize when evaporated, or when allowed to stand in a desiccator. Only a viscid syrup is produced. W. Crookes[19] observed that **thallous chromate,** $Tl_2CrO_4$, is precipitated when a soln. of a neutral thallous salt is treated with potassium chromate ; and also by digesting thallous dichromate with ammonia. E. Carstanjen obtained it from a soln. of thallous carbonate in aq. chromic acid. G. Canneri observed that M. Gröger's method for basic lead chromates yields with thallous salts, only the normal chromate. The action of dil. acid on thallous chromate yields thallous dichromate, but if a quantity of sulphuric acid insufficient to dissolve the chromate is employed and the boiling soln. is filtered and conc. **thallous hydrochromate,** $TlHCrO_4.Tl_2CrO_4$, in cinnabar-red crystals, and often in cruciform twins, is formed. Thallous chromate darkens when heated, and then melts without decomposition. At a higher temp. the salt decomposes. J. W. Retgers said that the crystals are probably not isomorphous with potassium chromate or thallous sulphate. According to G. Canneri, the e.m.f. of the electrode, mercury amalgam against a saturated thallous chromate soln. varies continuously with the temp., the curve exhibiting no characteristic point corresponding with the change in colour which thallous chromate crystals undergo when heated at 60°. Similarly the conductivity of sat. thallous chromate shows no sudden variation between 25° and 90°. The pale yellow or lemon-yellow amorphous precipitate is slightly soluble in water. E. Rupp and M. Zimmer said that 100 parts of water at 60° dissolve 0·03 part of thallous chromate ; and P. E. Browning and G. P. Hutchins said that 100 grms. of water at 100° dissolve 0·2 grm. E. Carstanjen observed that it is attacked by dil. hydrochloric acid ; and W. Crookes found that it is dissolved by moderately conc. boiling hydrochloric acid, and on cooling vermilion-red crystals separate—probably the trichromate. E. Carstanjen added that with conc. hydrochloric acid, thallous chloride is separated, and a green soln. is formed. W. Crookes also observed the formation of thallium chloride by the action of conc. hydrochloric acid. E. Carstanjen found that dil. sulphuric acid attacks thallous chromate slowly in the cold, and when the acid is heated, E. Willm said that the di- or tri-chromate is formed. With conc. sulphuric acid, violet thallium chrome-alum separates out. E. Carstanjen observed that dil. nitric acid, as well as conc. acetic acid, do not dissolve thallous chromate in

the cold, but with boiling soln., a little chromate is dissolved. It also behaves similarly towards aq. soln. of ammonia and sodium carbonate. M. Lachaud and C. Lepierre found that a litre of boiling *N*-KOH dissolves 3·5 grms. of thallous chromate, and on cooling, almost all separates out in six-sided pyramidal crystals. A soln. of potash-lye of sp. gr. 1·3 dissolves 18 grms. of chromate per litre. Molten potassium hydroxide converts it into thallic oxide. When thallous and potassium chromates are melted with potassium nitrate, **potassium thallous chromate,** $KTlCrO_4$, or $K_2CrO_4.Tl_2CrO_4$, is formed. M. Hebberling, and W. Strecker observed that reddish-yellow or brown precipitates are obtained when soln. of thallic salts are treated with soluble chromates or dichromates. The result is **thallic chromate.** According to G. Canneri, thallic chromate may be obtained pure as a golden yellow, crystalline powder by dissolving freshly-precipitated thallic oxide in excess of chromic anhydride soln. According to L. F. Hawley, **potassium thallic chromate,** $KTl(CrO_4)_2.2H_2O$, is obtained by adding potassium hydroxide to a soln. of thallic hydroxide in chromic acid. The yellow salt is rapidly hydrolyzed by water unless a large excess of chromic acid is present.

L. Haber [20] observed no precipitation occurs when cerium, lanthanum, and didymium salts are boiled with chromic acid, or with potassium or sodium dichromate, but a basic salt is precipitated when thorium or zirconium salts are similarly treated. J. F. John, and A. Beringer found that a soln. of cerous carbonate in aq. chromic acid slowly deposits **cerous chromate** as a yellow powder, and when the mother-liquor is evaporated, crystals of an acid salt are formed. According to S. Jolin, soln. of cerous salts also give precipitates of basic cerous chromates when treated with soln. of potassium chromate or dichromate. F. Zambonini and G. Carobbi found that when an intimate mixture of cerous chloride and potassium chromate is heated to 1000°, chromic oxide and cerium dioxide are formed. M. M. Pattison and J. Clarke found that when the chromates obtained by evaporating to dryness a soln. of the mixed oxides of cerium, didymium, and lanthanum in chromic acid, are heated to about 110°, only the cerium chromate is decomposed to form an insoluble powder, while the chromates of didymium and lanthanum remain unchanged. A. Brauell, and L. M. Dennis and B. Dales founded analytical processes on this reaction ; G. Krüss and A. Loose, and W. Muthmann and C. R. Böhm found that the fractional precipitation by potassium chromate of the ceria earths proceeds in the order : La, Pr, Nd, Sm ; and of the yttria earths, in the order : Tb, Yb, Er, Y, Gd. Processes of separation have been devised—by J. E. Egan and C. W. Balke, B. S. Hopkins and C. W. Balke, H. Moissan and A. Étard, C. R. Böhm, W. Muthmann and C. R. Böhm, L. M. Dennis and B. Dales, R. J. Meyer and J. Wuorinen, H. C. Holden and C. James, and C. James—based on this reaction—*vide* **5**. 38, 6. According to F. Frerichs and F. Smith, a soln. of lanthanum sulphate and potassium chromate gives a precipitate consisting of **lanthanum chromate,** $La_2(CrO_4)_3.8H_2O$. Lanthanum chromate is very liable to form a sparingly soluble potassium complex salt so that P. T. Cleve said that the precipitate probably contains the complex salt. The precipitate is yellow, granular, and consists of microscopic crystals. It is sparingly soluble in cold water and freely soluble in acids. P. T. Cleve obtained the octohydrate by treating a soln. of lanthanum nitrate with potassium chromate. H. T. S. Britton also prepared the *octohydrate* of lanthanum chromate by dissolving about 2 grms. of the rare earth in the minimum amount of chromic acid soln. ; diluting the liquid to 2 litres ; and gradually adding 0·1*M*-$K_2CrO_4$. When the amount of chromic acid used was kept sufficiently low, the quantity of potassium chromate required was small, thereby causing the simple chromate alone to be precipitated, but if too great a quantity of acid had been employed a correspondingly large amount of precipitant was necessary, and this often caused the precipitation of double chromates together with varying amounts of simple chromates. The salt is a bright yellow mass of microscopic, prismatic needles. 100 grms. of water at 25° dissolve 0·020 grm. calculated as anhydrous salt. The solubility is less at higher temp. F. Zambonini

and G. Carobbi obtained the anhydrous salt by heating the rare earth chloride and potassium chromate over 600°; and they obtained the *monohydrate*, $La_2(CrO_4)_3.H_2O$, by precipitation from cold soln. G. Carobbi studied the system $La_2(CrO_4)_3$–$(NH_4)_2CrO_4$–$H_2O$ at 25°—Fig. 52. The only complex salt formed was **ammonium lanthanum hexachromate,** $La_2(CrO_4)_3.3(NH_4)_2CrO_4.5H_2O$. The study of the system is complicated by the alteration of ammonium chromate into dichromate, so that when the ammonium chromate is in excess, ammonium dichromate crystallizes out, and when lanthanum chromate is in excess, the salt $La_2(CrO_4)_3.8H_2O$ separates. H. T. S. Britton obtained **potassium lanthanum tetrachromate,** $K_2CrO_4.La_2(CrO_4)_3.6H_2O$, as indicated above. P. T. Cleve found that if an excess of potassium chromate be employed, there is formed **potassium lanthanum heptachromate,** $4K_2CrO_4.La_2(CrO_4)_3.nH_2O$. G. Carobbi studied the system $La_2(CrO_4)_3$–$K_2CrO_4$–$H_2O$ at 25°, and found that the existence of the hydrated complex chromates, 1 : 1 : 2; 1 : 3 : 2; 1 : 4 : 2; 1·4 : 5 : 2; and 1 : 5 : 2, are indicated on the isothermal curve, Fig. 53. F. Frerichs and F. Smith obtained a precipitate resembling that with the lanthanum salt when a soln. of a didymium salt is treated with potassium chromate. The precipitated **didymium chromate,** $Di_2(CrO_4)_3.8H_2O$, was said by P. T. Cleve to be contaminated with a complex potassium salt which is obtained by treating a soln. of didymium nitrate with an excess of potassium chromate. H. T. S. Britton also obtained the bright yellow *octohydrate* of **praseodymium chromate,** $Pr_2(CrO_4)_3.8H_2O$, as in the case of the lanthanum salt; 100 grms. of water at 25° dissolve the eq. of 0·021 grm. of

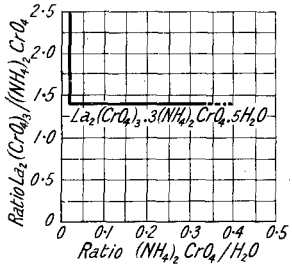



FIG. 52.—Equilibrium in the System: $La_2(CrO_4)_3$–$(NH_4)_2CrO_4$–$H_2O$ at 25°.

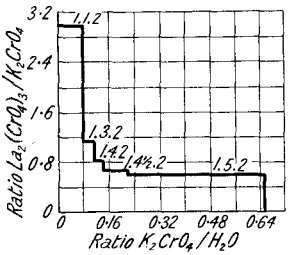



FIG. 53.—Equilibrium in the System: $La_2(CrO_4)_3$–$K_2CrO_4$–$H_2O$ at 25°.

the anhydrous salt. F. Zambonini also prepared the anhydrous salt, as well as the *decahydrate*, $Pr_2(CrO_4)_3.10H_2O$, by the methods indicated in connection with the anhydrous, and the monohydrated lanthanum salts. H. T. S. Britton likewise prepared the dull yellow *octohydrate* of **neodymium chromate,** $Nd_2(CrO_4)_3.8H_2O$, with a solubility of 0·027 grm. per 100 grms. of water at 25°. E. Baur said that this salt is olive-brown; and N. A. Orloff, moss-green. As in the case of the praseodymium salt, F. Zambonini and G. Carobbi also prepared the anhydrous salt, and the decahydrate. By adding an excess of potassium chromate to the soln. of a didymium salt, P. T. Cleve obtained yellow **potassium didymium chromate,** $K_2CrO_4.Di_2(CrO_4)_3.nH_2O$. It is hydrolyzed when washed with water with the loss of potassium chromate. H. T. S. Britton obtained a mixture of a basic chromate and **potassium praseodymium chromate** by adding an excess of potassium chromate to a chromic acid soln. of praseodymia; and similarly with **potassium neodymium chromate.** H. T. S. Britton obtained the *octohydrate* of **samarium chromate,** $Sa_2(CrO_4)_3.8H_2O$, as in the case of the lanthanum salt; 100 grms. of water at 25° dissolved 0·043 grm. of the salt calculated as anhydrous. F. Zambonini and G. Carobbi prepared the anhydrous salt and the *enneahydrate*, $Sa_2(CrO_4)_3.9H_2O$, as in the case of the anhydrous and monohydrated lanthanum salts. By adding potassium chromate to a soln. of a samarium salt, P. T. Cleve obtained a yellow, crystalline precipitate of **potassium samarium chromate,** $K_2CrO_4.Sa_2(CrO_3)_3.6H_2O$. No precipitation occurs with potassium dichromate. H. T. S. Britton found that

with an excess of potassium chromate the composition of the yellow flocculent precipitate varied with the composition of the precipitant; a complex salt is probably formed. The application of the phase rule is required to establish the nature of the complex salts. In general, the addition of a soln. of potassium chromate to an aq. salt soln. causes the precipitation of (*a*) in the case of lanthanum, the simple chromate if the excess of precipitant is small, (*b*) praseodymium, the simple chromate, (*c*) neodymium, a mixture of simple and basic chromates, (*d*) samarium, a basic chromate of indefinite composition. H. T. S. Britton continued: The only normal chromates which have been found hitherto belong to the cerite-group, the bases of which are believed to be among the strongest of the rare earths. Even among the members of this group there is a gradually increasing tendency to form basic chromates in the case of the weaker bases, neodymia and samaria.

G. Krüss and A. Loose, and W. Muthmann and C. R. Böhm obtained precipitates of **terbium chromate,** and of **gadolinium chromate** by adding potassium chromate to soln. of the corresponding salts. P. B. Sarder obtained the complex **potassium gadolinium chromates,** $K_2CrO_4.Gd_2(CrO_4)_3.7H_2O$, and $5K_2CrO_4.2Gd_2(CrO_4)_3.10H_2O$. G. Jantsch and A Ohl prepared **dysprosium chromate,** $Dy_2(CrO_4)_3.10H_2O$, as a sparingly soluble precipitate, by the interaction of soln. of the nitrate and of potassium chromate. The greenish-yellow, crystalline powder is soluble in water—at 25°, 100 c.c. of the soln. contain 1·0002 grms. of salt. When heated to 150°, the chromate loses 3·5 mols. of water; and at 150°, it decomposes. N. J. Berlin said that a basic yttrium chromate is formed when a soln. of chromic acid is sat. with yttria. The brown soln. deposits a brown powder. The salt was also obtained by O. Popp, G. Krüss and A. Loose, and W. Muthmann and C. R. Böhm. J. F. John observed that a soln. of yttrium carbonate in aq. chromic acid deposits orange-yellow crystals, of **yttrium chromate,** $Y_2(CrO_4)_3.nH_2O$, easily soluble in water. N. J. Berlin said that the spontaneous evaporation of the soln. gives yellowish-brown deliquescent crystals. P. T. Cleve obtained **potassium yttrium chromate,** $K_2CrO_4.Y_2(CrO_4)_3.nH_2O$, as a yellow, crystalline powder, by the action of potassium dichromate on yttrium carbonate. G. Krüss and A. Loose, and W. Muthmann and C. R. Böhm also prepared **erbium chromate,** and **ytterbium chromate.**

According to S. M. Godon de St. Menin,[21] when an aq. soln. of chromic acid mixed with hydrated silicic acid is evaporated, a reddish-yellow powder—silicon chromate—is formed, insoluble in water, and is not decomposed at an elevated temp. It is highly probable that no compound is formed. G. A. Quesneville, however, said that very little silicic acid is taken up by the soln., and that all the chromic acid is removed by washing. M. Blondel found that a conc. aq. soln. of chromic acid dissolves titanic acid in amounts depending on the conc., and temp. of the soln., and on the previous history of the titanic acid. When a conc. soln. containing one part of titanic oxide and 4 parts of chromium trioxide is diluted with 8 parts of water at 50° or 6 parts of water at 100°, **titanium tetroxychromate,** $3TiO_2.2CrO_3.H_2O$, or $TiO_2.2(TiO)CrO_4.H_2O$, is precipitated; with 25 parts of cold water, or 8 parts of water at 100°, **titanium trioxychromate,** $TiO_2.(TiO)CrO_4.2H_2O$, is produced; while with 50 parts of cold water or 12 parts of water at 100°, **titanium pentoxychromate,** $2TiO_2.(TiO)CrO_4.3H_2O$, is formed. On adding an eq. of ammonia to the same conc. soln. of the two oxides, $TiO_2.(TiO)CrO_4.2H_2O$ is precipitated, and the evaporation of the mother-liquor in vacuo yields hexagonal prisms of **ammonium titanium chromate,** $(NH_4)_2CrO_4.Ti(CrO_4)_2.H_2O$. All this has not yet been verified. M. Weibull found that **zirconium chromate** is precipitated when a zirconium salt soln. is treated with chromic acid or a dichromate. The flocculent, orange-red precipitate is sparingly soluble in dil. acids; and when washed with water chromic acid passes into soln. L. Haber said that the composition of the precipitate is indefinite. F. P. Venable and L. V. Giles, however, said that a definite salt $2ZrO(OH)_2.ZrOCrO_4.8H_2O$, **zirconyl tetrahydroxychromate,** is produced as a granular, yellow precipitate by dissolving zirconium hydroxide in a boiling soln. of chromic acid, diluting, and again boiling the soln. The compound obtained loses

a considerable quantity of its water at 110°, but the whole of it is lost only at 200°. It is suggested that its formation occurs as follows : first, normal zirconium chromate is formed, which is immediately hydrolyzed to $ZrOCrO_4$ ; some of the zirconium hydroxide is partly dehydrated to give $ZrO(OH)_2$. These two substances then combine to give the yellow insoluble basic salt. According to P. Krishnamurti and B. B. Dey, the addition of a large excess of a sat. soln. of potassium dichromate to a conc. soln. of zirconium oxychloride precipitates **zirconium octohydroxychromate,** $Zr_3(OH)_8(CrO_4)_2$ ; with a dil. soln. of the zirconium salt, **zirconium hexahydroxychromate,** $Zr_2(OH)_6CrO_4$, is formed ; and with very dil., boiling soln. of the oxychloride, and only a slight excess of dichromate, the product washed with boiling water corresponds with **zirconium decahydroxychromate,** $Zr_3(OH)_{10}CrO_4$. S. H. C. Briggs added a soln. of 7 grms. of crystalline zirconium nitrate in 50 c.c. of water to 10 grms. of potassium dichromate in 80 c.c. of water, after a day, the precipitate was filtered off, washed with a little water, and dried in vacuo, 2·5 grms. of the dried powder was heated in a sealed tube at 190° for 3½ hrs. with 6 grms. chromic trioxide, and 6 c.c. of water. The orange-red, homogeneous, insoluble, crystalline powder had the composition of **zirconium hexacosioxypentachromate,** $9ZrO_2.5CrO_3.12H_2O$, or $13ZrO_2.5Zr(CrO_4)_2.24H_2O$.

W. Muthmann and E. Baur [22] found that if a soln. of potassium chromate is dropped carefully into a boiling soln. of commercial thorium nitrate, first thorium will be precipitated completely as chromate and afterwards some rare earths begin to appear, indicated by a change in colour of the precipitate. This is the principle of E. Baur's method of separating the rare earths—*vide supra*. C. Palmer obtained **thorium chromate,** $Th(CrO_4)_2.H_2O$, by allowing a soln. of freshly precipitated thorium hydroxide in aq. chromic acid to stand for some time, or by mixing boiling soln. of a mol of thorium nitrate and 2 mols of potassium dichromate. The *monohydrate* appears as an orange-red, crystalline powder. He also prepared the *trihydrate* by evaporating in vacuo a soln. of freshly precipitated thorium hydroxide in a cold soln. of chromic acid. L. Haber prepared it as an orange-yellow, crystalline powder by boiling thorium nitrate for some time with aq. chromic acid, or better with sodium or potassium dichromate. Under similar conditions no precipitate is formed with cerium, lanthanum, or didymium salts. J. J. Berzelius said that the precipitated thorium chromate dissolves in an excess of chromic acid. The orange-yellow, rhombic plates lose their water of crystallization at 180° ; and they dissolve in moderately conc. mineral acids. J. Chydenius obtained yellow crystals of the *octohydrate* by evaporating over sulphuric acid a soln. of thorium hydroxide in aq. chromic acid, or an aq. soln. of thorium chloride and chromic acid. The salt loses its combined water at 100°, and the aq. soln. does not become turbid when boiled. C. Palmer also obtained **thorium dihydroxychromate,** $Th(OH)_2CrO_4$, by mixing a soln. of a mol of thorium nitrate and one of 3 mols of potassium chromate ; the precipitate first formed dissolves. The soln. furnishes golden-yellow crystals of the basic salt. According to H. T. S. Britton, if thorium hydroxide is suspended in a dil. soln. of chromic acid, it will be converted gradually into the normal chromate, the change occurring more rapidly on boiling. No basic salt of definite composition has been found. The composition varies, gradually approaching that of the normal chromate, but the conversion is complete only after long boiling. Crystals may appear to be slightly basic owing to the adsorption of normal chromate. The so-called basic thorium chromates are really mixtures of thorium hydroxide and thorium chromate. In other words, these basic chromates may be regarded as so-called adsorption compounds, or, taking into account the slight solubility of the normal thorium chromate, as having been produced by the simultaneous precipitation of both the hydroxide and the chromate. The basic chromate of C. Palmer is a special case of such a mixture. When soln. of thorium salts, to which potassium chromate has been added in quantities insufficient to give a permanent precipitate owing to the acid liberated by hydrolysis, are allowed to stand at room temp., if the conc. is sufficiently great, crystals of thorium chromate

trihydrate will be deposited slowly; but deposition occurs almost immediately from the boiling soln. The solubility of thorium chromate in soln. of chromic acid at 25°, when the composition is represented in percentages by weight, is as follows:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $CrO_3$ | 0·033 | 13·09 | 39·49 | 40·23 | 52·60 | 61·38 | 61·84 | 62·78 |
| $ThO_2$ | 0·044 | 6·52 | 24·22 | 23·04 | 7·91 | 17·65 | 6·27 | 0 |
| | $Th(CrO_4)_2.3H_2O$ | | | $Th(CrO_4)_2.CrO_3.3H_2O$ | | | $CrO_3$ | |

The results are plotted in Fig. 54. The compound **thorium chromatobis-chromate,** $Th(CrO_4)_2.CrO_3.3H_2O$, is better represented by this formula than by $Th(Cr_2O_7)(CrO_4).3H_2O$, because it can exist in equilibrium only with highly conc. soln. of chromic acid. It is decomposed by water.

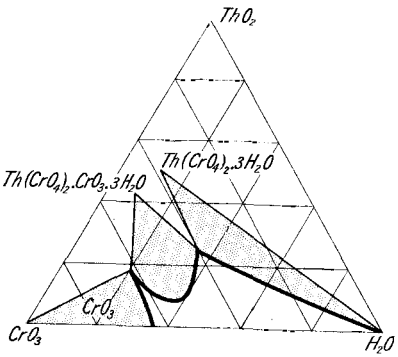



FIG. 54.—Equilibrium Diagram of the System: $ThO_2$–$CrO_3$–$H_2O$ at 25°.

According to J. J. Berzelius,[23] when stannous chloride is added to an excess of a soln. of potassium chromate, and the liquid agitated, yellow, curdy flocks of **stannous chromate** are precipitated; but if to a soln. of stannous chloride a dil. soln. of potassium chromate be added in small portions at a time, with constant agitation, a greenish precipitate of *chromic stannate* is formed. If the soln. of the tin-salt contains free acid, no precipitate is formed, and the soln. is green. P. Grouvelle obtained a similar result. According to J. J. Berzelius, stannic chloride soln., not containing free acid, gives a yellow precipitate of **stannic chromate,** when treated with potassium chromate. The supernatant liquor acquires an orange-yellow colour in consequence of the liberation of chromic acid. The dried precipitate is brownish-yellow, and when ignited forms violet *chromic stannate.* T. Leykauf said that if stannic chromate be heated to bright redness, a violet mass is obtained which communicates to pottery glazes colours ranging from rose-red to violet. F. J. Malaguti studied the *minéral lac,* or *laque minérale,* obtained by igniting 50 parts of stannic oxide with one part of chromic oxide. The pink or crimson colour develops more easily if calcium carbonate is a constituent of the ignited mixture. This is essentially the *chrome-tin pink* pottery colour. The pink coloration is probably the colour of highly dispersed chromic oxide, and the stannic oxide acts as a mordant. Other inert oxides can be used, but stannic oxide resists attack by the pottery glaze—*vide supra,* chromic oxide. This subject was studied by H. Stein, G. Steinbrecht, C. Lauth and G. Dutailly, H. A. Seyer, A. S. Watts, R. C. Purdy and co-workers, F. Rhead, W. A. Hall, and W. A. Lethbridge.

The mineral described by M. W. Lomonosoff,[24] J. G. Lehmann, and P. S. Pallas as *nora minera plumbi;* by J. G. Wallerius, as *minera plumbi rubra;* by A. G. Werner, as *Rothes Bleierz;* and L. C. H. Macquart, as *plomb rouge,* was found by L. N. Vauquelin, in 1757, to contain a new element in the form of chromate so that R. J. Haüy called it *plomb chromaté.* J. F. L. Hausmann proposed the name *kallochrom;* W. H. Miller, *lehmannite;* F. S. Beudant, *crocoise*—from κρόκος, saffron; F. von Kobell, *crocoisite;* and A. Breithaupt, **crocoite** (*Krokoit*), which was afterwards adopted by F. von Kobell and others. Analyses of the mineral by C. H. Pfaff,[25] J. J. Berzelius, C. Bärwald, and A. Liversidge; and of artificial preparations by J. J. Berzelius, H. Golblum and G. Stoffella, M. Gröger, A. J. Cox, N. S. Manross, L. Bourgeois, M. Lachaud and C. Lepierre, and C. Lüdeking, agree that the product is **lead chromate,** $PbCrO_4$.

L. N. Vauquelin, and J. J. Berzelius obtained normal lead chromate by precipi-

tation from a soln. of lead nitrate or acetate by the addition of potassium chromate or dichromate. The precipitate is yellow, and, according to E. F. Anthon, the colour is paler when precipitated from cold soln. than from hot soln., since the former is more or less hydrated; while L. N. Vauquelin said that a trace of potassium chromate in the precipitate darkens the colour. C. O. Weber, and M. Dullo discussed the effect of an excess of lead—*vide infra*. L. Dede and P. Bonin said that the precipitation is incomplete in acetic acid soln. if much chloride be present. Z. Karaoglanoff and B. Sagortscheff found that with lead chloride as the soluble lead salt, some $Pb_2Cl_2(CrO_4)$ is formed. The above mode of preparation, using the potassium or sodium chromates or chromic acid as precipitants, and soln. of varying degrees of concentration, were used by T. Gobel, F. G. Kidd, P. Jannasch, H. Golblum and G. Stoffella, J. Milbauer and K. Kohn, M. Fraudel, J. G. Gentele, E. Guignet, F. Rose, A. J. Cox, F. Auerbach and H. Pick, O. Meyer, M. Gröger, P. Breteau and P. Fleury, A. de Schulten, and G. Zerr and G. Rübencamp. J. Massignon and E. Watel obtained lead chromate by the action of soln. of lead salts on calcium chromate. G. N. Ridley showed that the precipitate formed on mixing aq. soln. of lead acetate and potassium dichromate is finer grained when the soln. are more dilute; but temp. has little influence on the fineness of grain. Precipitated lead chromate is amorphous. M. Lachaud and C. Lepierre found that the amorphous chromate is readily crystallized by boiling, say, 5 grms. with a soln. of 20 grms. of chromic acid in 70 grms. of water; L. Bourgeois boiled the precipitated chromate with dil. nitric acid (1 : 5 or 6), filtered the hot decanted liquid through glass-wool, and allowed it to cool slowly; he also obtained well-defined crystals by heating the chromate in a sealed tube at 150°. C. Lüdeking, and G. Cesaro allowed a soln. of lead chromate in potash-lye to stand exposed to the air. G. N. Ridley found that in alcoholic soln., precipitation is slow; and that the addition of an alcoholic soln. of potassium dichromate to a glycerol soln. of lead acetate produces only a slight turbidity—but precipitation occurs when water is added. No precipitation occurs in carbon disulphide soln.

Lead chromate was prepared by J. von Liebig, B. Legg, E. F. Anthon, M. Riot and B. Declisse, A. Scheurer, H. Hetherington and W. A. Allsebrook, and C. O. Weber by the action of soln. of the alkali chromates on lead sulphate. J. A. Atanasiu found that the electrometric titration of soln. of lead nitrate and potassium chromate gives a curve with a break corresponding with normal lead chromate. J. Milbauer

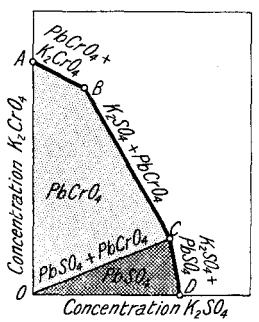



FIG. 55.—Isothermal Diagram for the System: $PbSO_4+K_2CrO_4 \rightleftharpoons K_2SO_4+PbCrO_4$.

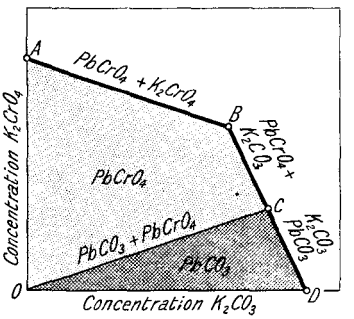



FIG. 56.—Isothermal Diagram for the System: $PbCO_3+K_2CrO_4 \rightleftharpoons K_2CO_3+PbCrO_4$.

and K. Kohn observed that the reaction: $PbSO_4+K_2CrO_4 \rightleftharpoons K_2SO_4+PbCrO_4$ progresses from left to right rapidly, and from right to left, slowly. The velocities of the reactions increase with temp. The equilibrium constant $K=[K_2CrO_4]/[K_2SO_4]$ is 0·000277 at 20°; 0·000365 at 40°; 0·000440 at 70°; and 0·000505 at 98·5°. No evidence of the formation of double salts was observed. The isothermal diagram has the form shown in Fig. 55, where *A* represents the solubility of potassium

chromate; and *D*, that of potassium sulphate. The regions of stability of the solid phases $PbCrO_4$, and $PbSO_4$ are shaded in the diagram. The curve *AB* represents a system in equilibrium with the four phases—$PbCrO_4$, $K_2CrO_4$, soln. and vapour; *BC*, a system in equilibrium with the four phases $PbCrO_4$, $K_2SO_4$, soln. and vapour; and *CD*, a system with the four phases $PbSO_4$, $K_2SO_4$, soln. and vapour in equilibrium. The four salts cannot exist side by side in the presence of their sat. soln. as the system would be invariant—**1**. 9, 5. At the point *C* there are six phases, $PbCrO_4$, $K_2CrO_4$, $K_2SO_4$, $PbSO_4$, soln. and vapour, in equilibrium. Adsorption is very marked at the low temp. and high concentration. It is inferred that the manufacture of chrome-yellow can be carried out from lead sulphate, and that various shades can be obtained by varying the conditions, temp., conc., and time. In the manufacture, an excess of lead acetate should be used, to secure the absence of adsorbed potassium chromate in the product, otherwise this chromate would rapidly convert the lead sulphate which is necessary for the particular shade, into lead chromate, and so the shade would be changed. J. G. Gentele's theory which explains the stability of chrome-yellow by the existence of a lead sulphatochromate is unlikely, since the present experiments make the existence of these double salts extremely doubtful.

F. Kuhlmann, C. O. Weber, and A. Winterfeld obtained lead chromate by the action of potassium chromate or dichromate on white-lead, or lead carbonate. H. Golblum and G. Stoffella studied the system: $PbCO_3+K_2CrO_4 \rightleftharpoons PbCrO_4+K_2CO_3$. The product nearly always contains a little lead carbonate. The isothermal diagram shown in Fig. 56, is analogous to that for the system indicated in the preceding diagram, Fig. 55. The mixture on the right of the equation $PbCO_3+K_2CrO_4 \rightleftharpoons PbCrO_4+K_2CO_3$, is more stable than that on the left. The equilibrium constant, $K=[K_2CO_3]/[K_2CrO_4]$, decreases with dilution on account of the disturbing effect of ionization. No compound or solid soln. of potassium chromate and lead chromate is formed, but the solubility of potassium carbonate decreases as the amount of lead carbonate in the solid residue and in soln. increases. A double compound of $K_2CO_3.PbCO_3$ appears to exist. The constant *K* at 25° is 5·46, and at 40°, 3·405. The thermal value of the reaction: $PbCO_3+K_2CrO_4=PbCrO_4+K_2CO_3$ is 5·822 Cals. If the equilibrium constant, *K*, Fig. 57, be represented by $K=Oa$, and the soln. of lead nitrate be added to a mixed soln. of potassium carbonate and chromate, when the ratio of $CO_3 \mid CrO_4$ is *greater* than *Oa*, lead carbonate alone will be precipitated until the ratio of the constituents remaining in soln. is equal to *Oa*; and conversely if the ratio be *less* than *Oa*, lead chromate alone will be precipitated. If the ratio be equal to *Oa*, and more than *Ob* of lead nitrate be added, a mixture of lead carbonate and chromate will be precipitated. On adding lead nitrate soln. to a mixed soln. of potassium chromate and carbonate, the precipitation of lead chromate or carbonate does not take place in such a way as to produce the predetermined ratio in the dissolved potassium salts. Whilst the interaction of lead carbonate and potassium chromate proceeds smoothly to an equilibrium, the interaction of lead chromate and potassium carbonate presents periodic phenomena. The curve representing the amount of potassium chromate formed oscillates with decreasing amplitude until the equilibrium is finally attained. This is attributed to the formation of a basic chromocarbonate of lead. On boiling lead chromate in potassium carbonate soln., a rhombic, ruby-red, crystalline solid is obtained with the composition: $3PbO.2CrO_3.2PbCO_3$. O. Ruff and E. Ascher studied the joint precipitation of lead and barium chromates; and lead sulphate and chromate; and O. Ruff, the X-radiograms.

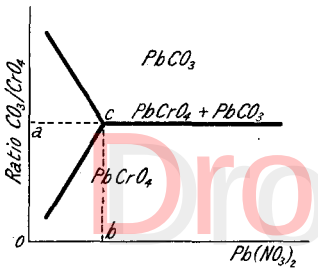



FIG. 57.—Mutual Precipitation of Lead Chromate and Carbonate.

N. S. Manross obtained crystals of lead chromate by melting lead chloride with potassium chromate, and leaching out the lead chloride, with boiling water. L. Bourgeois said that the yield is small because of the formation of the complex salt, $PbCl_2.PbCrO_4$. A better result is obtained by using potassium dichromate, but even then the result is not satisfactory. B. Redlich treated lead hydroxide with a soln. of sodium chromate or dichromate. The tint of the product is influenced by the presence of acetic acid, sodium sulphate, etc. F. Auerbech and H. Pick obtained lead chromate by treating basic lead chromate with a dil. aq. soln. of sodium hydrocarbonate and chromate; and M. Gröger, by the action of water on potassium lead chromate. D. G. Fitzgerald and R. C. Molloy roasted chromic oxide or chromite with lead oxide; and J. Milbauer said that there is a 100 per cent. conversion to chromate when a mixture of chromic oxide and lead oxide or carbonate is heated to 480° in oxygen at 12 atm. press. G. Chancel obtained lead chromate by warming a soln. of chromic oxide in alkali-lye with lead dioxide, and treating the filtrate with acetic acid. H. Vohl heated lead nitrate and chromic oxide in a crucible; and K. Toabe treated lead with a soln. of chromic and nitric acids at 60° to 140°. A. C. Becquerel obtained crystals of the salt by placing a Pb–Pt-couple in a soln. of chromic chloride in a sealed tube.

C. Lückow prepared lead chromate by an electrolytic process. The electrodes are formed of soft lead and the electrolyte is composed of a 0·3 to 3·0 per cent. soln. of sodium chlorate (perchlorate, nitrate, or acetate) 80 parts and sodium chromate 20 parts. The current density was 0·5 amp. per sq. dm. The colour of the deposit varies with the nature of the soln., being yellow in an acidic soln., and inclining to red in an alkaline soln.; electrodes about 10 to 20 mm. apart, and 1·5 to 1·6 volts are needed for weakly acid soln.; about 1·7 volts for neutral soln., and 2 volts for weakly alkaline soln. M. le Blanc and E. Bindschedler found that in the electrolysis of soln. of sodium chlorate and chromate, containing 1·5 to 12 per cent. of salt—of which 70 to 90 per cent. is chlorate—by means of a lead anode, lead chromate is formed near the anode, separating from it by its own weight, whereas in soln. containing a large proportion of chromate an adherent layer of chromate and lead dioxide forms on the anode. The yield of lead chromate is theoretical in the first case, practically zero in the latter. Sodium nitrate, acetate, or butyrate give practically the same result as chlorate. With the mixed electrolyte, the current is mainly transported by $ClO'_3$-ions, the chromate ions are therefore soon removed almost completely from the electrolyte in contact with the anode, and the precipitation of lead chromate takes place at some small distance from it. With a more conc. chromate soln., this is not the case. K. Elbs and R. Nübling found that in the electrolysis of very dil. soln. of chromic acid with lead electrodes, lead chromate alone is obtained; with more conc. soln.—up to 40 or 50 per cent.—there is evidence of the formation at the anode of **plumbic chromate,** $Pb(CrO_4)_2$, or of a mixture of lead chromate and dioxide; and with very conc. soln.—130 grms. of $CrO_3$ per 100 c.c.—a soln. is obtained which evolves oxygen when kept and deposits lead dichromate. The quantity of oxygen evolved is in agreement with $Pb(Cr_2O_7)_2 = PbCr_2O_7 + 2CrO_3 + O$. According to G. Just, the potential difference between a lead anode and a soln. containing bivalent lead ions depends very much on the anodic current density (probably owing to local increase of the conc. of the lead ions) so that at high current densities it may rise to the normal value for lead dioxide. When this is the case, lead dioxide is, of course, formed on the anode. B. Huick electrolyzed a 1·5 per cent. soln. of a mixture of sodium chlorate (95 parts) and sodium dichromate (5 parts) for lead chromate.

As pointed out by E. E. Free, by using very dil. soln. of lead nitrate and potassium chromate—say *M*- to $\frac{1}{256}M$-soln.—yellow **colloidal solutions** are obtained which are stable for some days; and, if glue be present, the soln. are stable for many months. J. Milbauer and K. Kohn also found that in the presence of acetic acid, or when boiled, the colloidal lead chromate is flocculated. F. W. O. de Coninck observed that when crystalline lead chromate is boiled for one-half to one hour

with a very conc. soln. of pure potassium nitrate and immediately filtered, the filtrate exhibits a well-marked red fluorescence and contains lead chromate. If, however, the filtrate after some moments is refiltered, the filter retains the lead chromate, and the second filtrate is colourless. Sodium nitrate behaves similarly, but much more slowly. It is thus inferred that the lead chromate is rendered colloidal by the nitrate soln. but that the colloidal form re-polymerizes very rapidly. W. Lenze obtained colloidal soln. by mixing 25 grms. of a 10 per cent. soln. of sodium protalbinate (or lysalbinate) with 15 grms. of a 20 per cent. soln. of lead acetate, and treating a soln. of the precipitate in soda-lye with a conc. soln. of potassium chromate, and adding enough acetic acid to prevent precipitation. The soln. was dialyzed. It is greenish-yellow in reflected light, and brown, in transmitted light. J. N. Mukherjee and H. L. Ray studied the adsorption of salts by precipitated lead chromate.

A. Drevermann obtained crystalline lead chromate by the very gradual diffusion of very dil. soln. of potassium chromate and lead nitrate into water. The solids were placed in separate cylinders, placed in a wide dish, and the dish filled with water above the tops of the cylinders. If air is present, some basic salt may be precipitated. L. Bourgeois said that besides the crystalline chromate some amorphous basic chromate may be precipitated. H. Vohl also obtained the crystals by allowing soln. of a lead salt and a chromate to diffuse into each other through a porous *diaphragm*. E. Hatschek studied the **rhythmic precipitation** of lead chromate. A small quantity of 0·5 per cent. soln. of potassium dichromate is introduced into a tube containing a one per cent. agar-agar jelly containing 0·1 per cent. of lead acetate. The diffusion of the soln. into the jelly is accompanied by the formation of a stratified system. If a second small quantity of dichromate is added when the first has completely disappeared, it is found that the diffusion of the newly-added dichromate gives rise to a second system of strata, in which the successive bands are much broader than those in the first system. The fact that two different systems can be obtained in the same jelly is considered to be irreconcilable with the supersaturation theory which has been advanced to account for the formation of these stratified systems. The subject was investigated by R. E. Liesegang, E. R. Riegel and L. Widgoff, S. C. Bradford, E. Hatschek, P. B. Ganguly, V. Moravek, A. C. Chatterji and N. R. Dhar, D. N. Ghosh, and K. Ando.

The mineral crocoite occurs crystalline, and in imperfectly columnar or granular masses coloured various shades of bright hyacinth-red, or orange-red. The crystals are feebly pleochroic. The **colour** of the artificial crystals is also orange-red. When the crystals are finely powdered, the colour is yellow, like that of the precipitated cryptocrystalline or amorphous powder. Normal lead chromate, prepared by precipitation, is a clear yellow and its use as a pigment explains why so many investigations have been made on processes of manufacture with the object of increasing the purity and clarity of the colour of *chrome-yellow*—light, medium, and dark. Some of these terms are also applied to other chromate yellows, *jaune de chrome*, *giallo di cromo*, *amarillo de cromo*, or *Chromgelb*—light, medium, and dark. It also has the trade-names *Paris yellow*, *King's yellow*, a term also applied to orpiment. The paler tints—*lemon-chrome*, and *citron-chrome*—are produced by mixing lead chromate with lead sulphate. By increasing the basicity of the chromate the colour is deepened, and reddened; so that an unbroken series of colours can be obtained varying from the pure yellow of the normal chromate to the deep orange-red of the basic salt—*orange-chrome*, *chrome-red*, which also has the trade-names *chrome-cinnabar*, *chrome-garnet*, *chrome-ruby*, *Austrian red*, *Vienna red*, *Derby red*, *American Vermilion*, *rouge de Perse*, etc. The variations of colour among different samples of the same compound may be greater than with different compounds. The variation in colour may be due to differences in the basicity, hydration, average grain-size, etc.; and it is conditioned by the temp., and conc. of the soln., by the time occupied in the precipitation; and by the nature of the soln. which in turn affects the salts adsorbed by the precipitated chromate. The

subject was discussed by J. Milbauer and K. Kohn, L. Bock, C. O. Weber, K. Jablczynsky, J. W. Bain, F. Rose, G. Zerr, G. Zerr and G. Rübencamp, E. Guignet, J. G. Gentele, and J. Bersch. E. E. Free said that for clear yellow colours, the formation of basic salts must be avoided. The presence of a slight trace of alkali, or a higher temp. than usual, may cause a darkening of the yellow colour. This darkening is produced by a number of unrecognized causes, but P. Grouvelle, and M. Dullo considered that in many cases the alteration of the colour is a visible sign that the normal chromate has undergone a partial change to the basic condition, produced by the presence of alkali. This is confirmed by the fact—observed by S. M. Godon de St. Menin, L. N. Vauquelin, C. O. Weber, and H. W. Hofmann—that the presence of small amounts of free acid in the soln. lessens the tendency for the colour to turn. C. O. Weber also noticed that an excess of chromate in the precipitating soln. favours the tendency of the colour to change, while an excess of lead salt acts in the converse way; but M. Dullo does not agree with this statement. E. E. Free suggested that in some cases the darkening of the colour may be due to the growth of the fine granules into coarser grains. The darkening of the colour may render the chrome-yellow quite useless for a pigment.

E. E. Free showed that the difference in the colour of the yellow colour of the powder and the orange colour of the crystals is due to differences in the grain-size. The largest crystals are obtained with hot dil. soln. The size of the precipitated crystals increases continuously with decrease in conc. The colours of the precipitates obtained from the most conc. and the most dil. soln. are lighter than is the case with precipitates from soln. of intermediate conc. The curve shows a maximum depth of colour at moderate conc. So that size of grain alone does not suffer to explain the results. It is assumed that the basicity as well as grain-size were concerned in the effects obtained. A. Habich, T. Gobel, and J. Bersch showed that the larger crystals of the basic chromates correspond with the deeper and redder shades of colour; and W. E. Fuss stated that chrome-red, when ground, acquires a yellow tinge. B. Redlich said that chromates prepared by the action of chromate soln. on lead hydroxide are redder when the hydroxide is crystalline. E. L. Nichols and B. W. Snow showed that the reflection spectrum of pigments is produced by light reflected from the surface, and by light reflected from the interior faces. That reflected from the surface is white; and that reflected from the interior determines the colour of the pigment. The internally reflected light is that light which has entered at least one of the crystals and been reflected from the posterior surface of that crystal or from the surface of some other crystal situated more deeply within the mass. E. E. Free continued: with a more finely powdered pigment, there will be obviously more surface per unit of mass, and the first of these interior faces will be on the average nearer the external surface of the layer, that is, the layer of coloured material through which the internally reflected ray must pass, is less in the finely powdered material. It must therefore happen that the selective absorption which takes place in this ray will be relatively weaker, or in common phrase the "colour" imparted to the ray will be less marked. Crystalline lead chromate, however, changes from a reddish-orange to a clear yellow when powdered; so that there appears to be not only a weakening of the colour, but an actual change from red or orange into yellow. E. L. Nichols found that when light is reflected from a thin plate of lead chromate, the blue and violet, most of the green, and a considerable fraction of the yellow are absorbed, but the red is allowed to pass in greater degree and in increasing proportion with increasing wave-length. This is

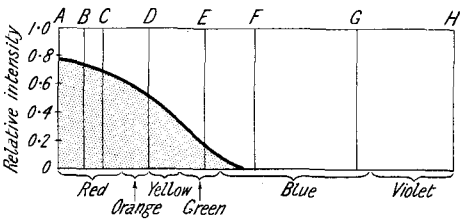



FIG. 58.—The Spectrum of Light Reflected from Lead Chromate.

shown by Fig. 58, where the abscissæ represent wave-lengths, and the ordinates of the intensities of the reflected light in terms of uniform white light. The green component of the light which reaches the eye is masked by the larger proportion of red, and the apparent colour is a shade of yellow or orange tinged with red. By increasing the thickness of the plate, the area representing the absorbed light extends towards the left, thus concentrating the red and reducing the yellow. Conversely when the thickness of the plate is decreased, the green progressively weakens the red and makes the yellow more prominent in the transmitted light. As the transmitted light extends into the blue, a further decrease in the thickness of the plate, the blue tends to neutralize the yellow, as the green neutralizes the red, and the yellow becomes paler and paler, until in the limiting case the colour appears white. L. Godard studied the effect of radiant heat rays by chrome-yellow. Lead chromate belongs to the class of substances which W. Ackroyd called metachromatic because they change their colour on heating. The colour was shown by R. F. Marchand, L. Bourgeois, and E. J. Houston and E. Thomson to change from yellow to orange to red, and in this respect, it behaves like the majority of other substances observed by C. F. Schönbein, and E. J. Houston and E. Thomson, in that the maximum intensity, with rise of temp., moves towards the red. The basic chromates also become a deeper red when heated. Conversely, as the yellow chromate is cooled to −30° to −40°, it becomes yellowish-green; and M. Bamberger and R. Grengg said that both the natural and artificial crystals are decolorized at −190°.

The **crystals** of crocoite are monoclinic prisms; and, according to H. Dauber, the axial ratios are $a:b:c=0{\cdot}9603:1:0{\cdot}9159$, and $\beta=102°\ 27'$; E. F. Chirva gave $a:b:c=0{\cdot}960293:1:0{\cdot}91305$, and $\beta=77°\ 32'\ 55''$. The crystals are usually prismatic, but the habit varies so that the crystals sometimes resemble acute rhombohedra. The faces are usually smooth and brilliant; the (110) face may be vertically striated. The (110)-**cleavage** is distinct; but the (001)- and (100)-cleavages are not so well defined. The crystals were also examined by N. von Kokscharoff, and F. Hessenberg. A. de Schulten, A. Drevermann, and L. Bourgeois also showed that the artificial crystals are monoclinic prisms. B. Gossner and F. Mussgnug showed that the **X-radiograms** correspond with $a=6{\cdot}82$ A., $b=7{\cdot}48$ A., $c=7{\cdot}16$ A., and $\beta=102°\ 33'$; or $a:b:c=0{\cdot}912:1:0{\cdot}957$. The vol. of unit cell is $356{\cdot}5\times10^{-24}$ c.c. G. Tammann and Q. A. Mansuri found that the recrystallization of the powder with granules less than 0·3 mm. begins between 237° and 248°. The **optical character** is positive; and the **optic axial angle** $2V=54°$. In accord with the dimorphism of lead sulphate, discussed by W. Grahmann, P. Groth and K. Haushofer said that lead chromate is probably dimorphous furnishing monoclinic and rhombic crystals. C. Lüdeking obtained artificially what he regarded as rhombic crystals—*vide supra*. According to F. M. Jäger and H. C. Germs, lead chromate is trimorphic. The monoclinic or $\alpha$-form is stable below 707°; the $\beta$-form is stable between 707° and 783°; and the $\gamma$-form between 783° and the m.p. 920°—Fig. 62. The transition $\alpha$-$PbCrO_4 \rightleftharpoons \beta$-$PbCrO_4$, at 707°, is attended by a small thermal change, while the transition $\beta$-$PbCrO_4 \rightleftharpoons \gamma$-$PbCrO_4$, at 783°, involves a greater thermal change. Some varieties of crocoite showed only one transition temp. at 792°.

C. H. D. Bödeker gave 5·951–6·004 for the **specific gravity** of lead chromate; L. Playfair and J. P. Joule, 5·653; and P. Niggli, 6·123. H. G. F. Schröder gave 5·965 for the sp. gr. of crocoite; and for the artificial crystals, N. S. Manross gave 6·118; A. de Schulten, 6·123 at 15°; L. Bourgeois, 6·29; J. Milbauer and K. Kohn gave 5·44 for that of the amorphous precipitate. B. Gossner and F. Mussgnug calculated 6·00 for the sp. gr. The **hardness** of crocoite is 2·5 to 3·0. P. W. Bridgman found the linear **compressibility** at 30°, in the direction $C$ of the monoclinic crystals, to be $\delta l/l_0=0{\cdot}0_64978p-0{\cdot}0_{11}378p^2$, and at 75°, $\delta l/l_0=0{\cdot}0_65102p-0{\cdot}0_{11}422p^2$ for press. $p$ ranging up to 12,000 kgrms. per sq. cm. H. Kopp gave 0·0900 for the **specific heat** between 19° and 50°; and 29·0 for the mol. ht. T. M. Lowry and L. P. McHatton observed that the fineness of the

powder produced by the decrepitation of crocoite depends on the proportion of included water which the mineral contains. R. F. Marchand said that lead chromate fuses at a red-heat and, on cooling, solidifies to a dark brown mass which forms a brownish-yellow powder; but if the molten chromate be poured into cold water, it forms a red mass which yields a red powder. F. M. Jäger and H. C. Germs found that the **melting point** of lead chromate is 844°—and fusion is attended by a little decomposition; while crocoite melts at 835° to 839°. R. F. Marchand said that when heated above its m.p., it gives off about 4 per cent. of oxygen forming lead dichromate and chromic oxide. The amount of oxygen evolved is only a fractional part of that which would be evolved if the decomposition were complete. R. F. Marchand represented the reaction: $4PbCrO_4=2Pb_2O(CrO_4)+Cr_2O_3+3O$; C. Schubert, and W. Hempel and C. Schubert found that the evolution of gas begins at about 600°, and he observed rather more oxygen is given off up to 1150° than is required by this equation. If re-heated in oxygen gas, the chromate is not reformed; but if a mixture of chromic oxide and lead oxide be heated in oxygen, 14·9 parts of oxygen are taken up for 100 parts of chromic oxide. W. Hempel and C. Schubert found that dissociation begins at about 600°, and is completed at 1150°. R. Lorenz and W. Herz studied some relations between the b.p. and the critical temp. H. C. Sorby gave 2·730 for the **index of refraction** of crocoite; C. Bärwald gave 2·203 and 2·667 for red-light, and 2·437 and 2·933 for green-light; while A. des Cloizeaux gave 2·42 for yellow-light. A. de Gramont examined the **spark spectrum** of crocoite. G. H. Hurst found that chrome-yellow reflects a large proportion of the yellow and green rays, with a small quantity of orange and blue rays, Fig. 59. G. I. Pokrowsky studied the polarization of light by finely divided lead chromate suspended in water. W. W. Coblentz gave for the diffuse reflecting power:

| | | | | | |
|---|---|---|---|---|---|
| λ . . | 0·54μ | 0·60μ | 4·4μ | 8·8μ | 24·0μ |
| Emission . | 61·2 | 70·2 | 41·2 | 4·74 | 7·4 |

T. W. Case said that the **electrical resistance** of crocoite exceeds one megohm, and is not affected by light. The sp. **electrical conductivity** of a sat. soln. at 18° was found by F. Kohlrausch to be of the order $0·1\times10^{-6}$ mhos. According to J. Rosenthal, the electrical conductivity of the compressed powder increases with temp., being 0·110 mho at 208°, and 0·385 mho at 331°. The precipitated powder is a better conductor than that obtained by grinding the fused chromate. R. Labes studied the electrical charges on the surface of lead chromate in soln. of electrolytes.

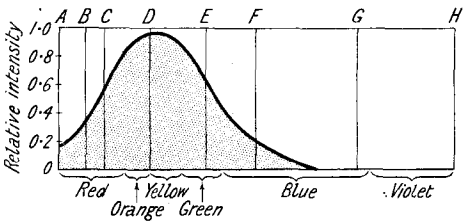



FIG. 59.—Reflection Spectrum of Chrome-yellow.

E. Rutherford and F. Soddy observed that red-hot lead chromate has no action on **radium or thorium emanation.** R. F. Marchand observed that when lead chromate is heated in **hydrogen,** water is formed and the mass becomes incandescent before the temp. of the vessel had attained a red-heat. The reaction is symbolized $2PbCrO_4+5H_2=5H_2O+Cr_2O_3+2Pb$. H. Mennicke found that hydrogen *in statu nascendi*—from hydrochloric acid and zinc in the presence of platinum—reduces lead chromate quickly and completely. J. Milbauer and K. Kohn said that when the yellow chromate is warmed with **water** it becomes red, but on cooling the yellow colour is restored; and A. J. Cox found that at 25°, the chromate is hydrolyzed so that the water contains about 0·02 millimol of chromic acid per litre. J. F. G. Hicks and W. A. Craig studied the progressive hydrolysis of lead chromate by water at 100° at ordinary press., and in sealed tubes; and found that the reaction is complete in about 3 hrs. A basic lead chromate is formed. The older

chemists thought that lead chromate is insoluble in water, but A. Drevermann found that 1000 parts of water dissolve 0·02 part of salt; and P. Harting said that lead nitrate is precipitated as chromate when one part is present in 70,000 parts of water. G. von Hevesy and F. Paneth gave for the solubility $1{\cdot}2\times10^{-5}$ grm. per litre at 25°; G. von Hevesy and E. Rona gave $2\times10^{-7}$ mol per litre at 20°; F. Kohlrausch and F. Rose, 0·0002 grm. per litre at 18°; F. Kohlrausch, 0·0001 grm. per litre at 18°; K. Beck and P. Stegmüller, $3\times10^{-7}$ mol per litre at 25°. F. Auerbach and H. Pick gave for the solubility product, $[Pb''][CrO_4'']=2\times10^{-14}$ at 18°; and $[Pb'']^2[CrO_4''][OH']^2=6\times10^{-35}$. P. Schützenberger observed that when heated in a porous crucible over a gas-flame, lead chromate adsorbs moisture which is expelled only at a red heat. K. B. Lehmann observed that conductivity water dissolves more than distilled water. According to L. N. Vauquelin, lead chromate dissolves completely in a soln. of **potassium hydroxide**; and F. Wöhler and J. von Liebig added that the soln., sat. while hot, deposits after a few days yellowish-red laminæ of a basic salt. A. Drevermann also said that a soln. of potassium hydroxide makes the crystals opaque, and darker, and they are then slowly dissolved. M. Lachaud and C. Lepierre found that a litre of 2*N*-KOH dissolves 11·9 grms. of lead chromate at 16°; 16·2 grms. at 60°; 26·1 grms. at 80°; and 38·5 grms. at 102°, forming $K_2Pb(CrO_4)_2$. Conc. potash-lye—say 45 per cent. KOH, sp. gr. 1·47—forms oxychromate, or lead monoxide; but 2*N*-KOH forms only the oxychromate. Molten potassium hydroxide forms crystals of the oxychromate—*vide infra*, basic salts. R. Eberhard observed that the salt is soluble in an alcoholic soln. of potassium hydroxide. According to F. Brandenburg, when lead chromate is boiled with a soln. of **potassium carbonate,** a basic oxychromate is formed, and then lead carbonate; the liquid takes up much chromic and lead oxides, and when treated with sulphuric acid, lead chromate is precipitated. The observations of H. Golblum and G. Stoffella on the equilibrium $PbCrO_4+Na_2CO_3\rightleftharpoons PbCO_3+Na_2CrO_4$ have been summarized in Fig. 60. K. B. Lehmann found that a dil. soln. of sodium carbonate readily dissolves lead chromate and a state of equilibrium is inaugurated with the oxychromate: $2PbCrO_4+2Na_2CO_3+H_2O\rightleftharpoons PbO.PbCrO_4+2NaHCO_3+Na_2CrO_4$. With increasing dilution and rise in temp. the equilibrium is displaced towards the right-hand side of the above equation. When the equilibrium is approached from the side of the basic lead chromate, exactly the same results are not obtained as from the side of the normal lead chromate. The reversible reaction expressed by the equation: $PbCrO_4+Na_2CO_3\rightleftharpoons PbCrO_3+Na_2CrO_4$, only takes place in the presence of considerable quantities of hydrocarbonate in soln., otherwise basic lead chromate is formed. For soln. with the total sodium conc. from 0·05*N*- to 0·1*N*-$Na_2CO_3$, at 18°, the equilibrium constant, for the reaction $2PbCrO_4+2CO_3''+H_2O\rightleftharpoons PbO.PbCrO_4+CrO_4+2HCO_3'$ is $[CrO_4''][HCO_3']^2/[CO_3'']^2=0{\cdot}057$—*CQ'*, Fig. 60; for $2PbCO_3+CrO_4''+H_2O\rightleftharpoons 2HCO_3'+PbO.PbCrO_4$, it is $[HCO_3']^2/[CrO_4'']=1{\cdot}95$—*Q'B*, Fig. 60; and for $PbCrO_4+CO_3''\rightleftharpoons CrO_4''+PbCO_3$, it is $[CrO_4'']/[CO_3'']=0{\cdot}2$—*AQ'*, Fig. 60; and if carbonic acid be present, $[H_2CO_3][CrO_4'']/[HCO_3]^2=4\times10^{-5}$. Lead chromate enters into reversible reaction with a soln. of sodium hydrocarbonate according to the equation: $PbCrO_4+2NaHCO_3\rightarrow PbCO_3+Na_2CrO_4+CO_2+H_2O$; equilibrium is attained at a much lower press. of carbon dioxide than is the case with lead sulphate. The equilibrium conditions for the ternary system: $Na_2CO_3$–$NaHCO_3$–

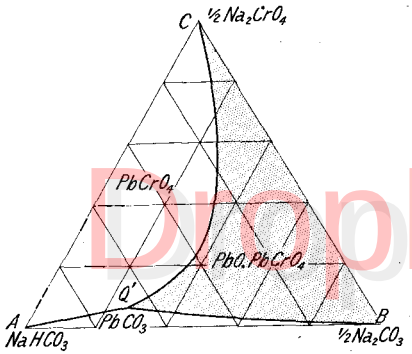



FIG. 60.—Equilibrium between Lead Chromate and 0·1*N*-Sodium Carbonate Solutions at 18°.

$Na_2CrO_4$ in the presence of lead chromate, oxychromate and carbonate, are shown in Fig. 60. The region where lead carbonate is stable is very small, and the transformation $PbCrO_4+Na_2CO_3 \rightleftharpoons PbCO_3+Na_2CrO_4$ occurs only in the presence of hydrocarbonate. The regions of stability of the two lead chromates are very wide.

H. Moissan observed that **hydrogen chloride** decomposes lead chromate forming red fumes of chromyl chloride; and H. Schwarz, that hot **hydrochloric acid** dissolves the chromate with the formation of chlorine, lead chloride, and chromic chloride. M. Gröger said that hot, dil. hydrochloric acid decomposes the chromate completely forming lead chloride which, if not filtered off, and water be added, re-forms lead chromate. K. Beck and P. Stegmüller found the solubility, $S$ millimols per litre, to be :

| HCl | | 0·1*N*- | 0·2*N*- | 0·3*N*- | 0·4*N*- | 0·5*N*- | 0·6*N*- |
|---|---|---|---|---|---|---|---|
| $S$ | 18° | 0·186 | 0·393 | 0·654 | 1·07 | 1·56 | 2·25 |
| | 25° | 0·239 | 0·485 | 0·839 | 1·32 | 4·06 | 2·95 |
| | 37° | 0·337 | 0·744 | 1·31 | 2·10 | 3·28 | 4·69 |

so that, as indicated by K. B. Lehmann, the solvent action is greater, the more conc. the acid. A conc. soln. of sodium chloride dissolves traces of the chromate; and M. Lachaud and C. Lepierre stated that molten sodium chloride converts the chromate into basic chromates. J. F. G. Hicks, and J. F. G. Hicks and W. A. Craig found that reactions in fused salts can be brought about to yield products analogous to those obtained with the same initial substances in aq. soln., the chief difference being the slowness of the reactions in the fused medium at 870°. The reaction with fused **sodium chloride** represents a true state of equilibrium. A basic chromate is the main product of the reaction. J. Milbauer and K. Kohn found that lead chromate reacts quantitatively with **potassium iodide :** $CrO_4'' + 8H' + 3I' = Cr''' + 4H_2O + 3I$. M. le Blanc and E. Bindschedler found lead chromate to be insoluble in contact with a 1·5 per cent. soln. of **sodium chlorate** for 4 hrs. at room temp. H. H. Willard and J. Kassner found that the solubility of lead chromate in **perchloric acid,** $S$ grm. per 100 c.c. at 25°, is :

| $M$-$HClO_4$ | 0·1 | 0·5 | 1·0 | 2·0 | 3·0 | 4·0 | 5·0 |
|---|---|---|---|---|---|---|---|
| $S$ | 0·0041 | 0·0120 | 0·0140 | 0·0199 | 0·0211 | 0·0213 | 0·0191 |

The solubility is reduced if lead perchlorate or sodium dichromate be present.

J. B. Senderens said that the chromate is not altered when boiled for a week with water and **sulphur.** The presence of free sulphur, or **sulphides,** gradually darkens chrome-yellow owing to the formation of lead sulphide. E. F. Anthon heated in a glass tube a mixture of lead chromate with one-eighth of its weight of sulphur, and found that the product takes fire with incandescence on exposure to air, forming sulphur dioxide, and chromic and lead oxides. H. Moissan and P. Lebeau said that **sulphur hexafluoride** is not decomposed by molten lead chromate. Hot sulphuric acid decomposes lead chromate, forming lead sulphate, and H. Schwarz found that for complete decomposition an excess of 4 to 5 mols of sulphuric acid is necessary; M. Gröger found that the decomposition with boiling dil. sulphuric acid is incomplete; the cold conc. acid acts slowly while the hot acid acts quickly, forming chromic acid. J. Milbauer and K. Kohn's observations on the reaction with **potassium sulphate** soln. are summarized in Fig. 55. G. Chancel said that lead chromate is insoluble in a soln. of **sodium thiosulphate.**

E. C. Franklin and C. A. Kraus found that lead chromate is insoluble in liquid **ammonia;** and W. E. Garrigues that it is insoluble in aq. ammonia. C. L. Parsons found that lead chromate favours the oxidation of ammonia by air. R. H. Brett said that the salt is insoluble in a soln. of ammonium chloride. A. Drevermann, J. von Liebig, and A. Baumann observed that lead chromate is insoluble in nitric acid. E. Duvillier stated that boiling conc. **nitric acid** dissolves 98·79 per cent. $CrO_3$ and only 1·21 per cent. PbO, while the remaining lead separates as lead

nitrate. When water is added to the mixture, lead chromate is reformed. K. Beck and P. Stegmüller gave for the solubility $S$ millimols Pb per litre, at 18°,

| $HNO_3$ | 0·1*N*- | 0·2*N*- | 0·3*N*- | 0·4*N*- | 0·5*N*- | 0·6*N*- |
|---|---|---|---|---|---|---|
| $S$ | 0·129 | 0·227 | 0·312 | 0·401 | 0·488 | 0·598 |

H. H. Willard and J. L. Kassner found the solubility of lead chromate, $S$ grm. per 100 c.c. at 25°, in nitric acid, to be :

| $M$·$HNO_3$ | 0·1 | 0·5 | 1·0 | 2·0 | 3·0 | 4·0 | 5·0 |
|---|---|---|---|---|---|---|---|
| $S$ | 0·0063 | 0·0177 | 0·0385 | 0·0889 | 0·1701 | 0·2812 | 0·4367 |

The solubility is reduced if lead nitrate, or sodium dichromate be present. C. Marie said that 0·5 grm. of lead chromate dissolves in a mixture of nitric acid with 2 grms. of **ammonium nitrate.** F. Wöhler and J. von Liebig found that molten **potassium nitrate** converts lead chromate into the oxychromate; and M. Lachaud and C. Lepierre observed the formation of the complex salts $K_2Pb(CrO_4)_2$ and $2PbO.K_2Pb(CrO_4)_2$. Similarly also with sodium and lithium nitrates. J. F. G. Hicks, and J. F. G. Hicks and W. A. Craig studied the reaction with an equimolar mixture of fused sodium and potassium nitrates at various temp. up to 230°. The reaction at different temp. represents states of equilibrium analogous to hydrolysis. The product of the reaction is a basic chromate. F. W. O. de Coninck studied the peptizing action of a boiling soln. of potassium nitrate on lead chromate—*vide supra.* K. Jellinek and H. Ens found that 3 drops of a one per cent. soln. of **silver nitrate** are coloured reddish-brown owing to the formation of silver chromate.

H. Moser observed that when heated with **carbon,** lead chromate is reduced to lead and chromic oxide. E. Berger and L. Delmas found that the combustion of carbon in air is facilitated by the presence of lead chromate. M. Tarugi found that at 400°, **calcium carbide** reduces the chromate to a calcium lead alloy and chromium. A. Kutzelnigg observed that lead chromate exerted an oxidizing action on a soln. of **potassium ferrocyanide ;** and J. R. Campbell and T. Gray, that the salt exerts an oxidizing action on **methane** and **ethylene.** K. B. Lehmann found that conc. **acetic acid** dissolves very little lead chromate ; and A. Baumann, that acetic acid dissolves no chromate. Lead chromate is almost insoluble in a soln. of **ammonium acetate ;** and, according to I. M. Kolthoff, in a soln. of **sodium acetate.** H. C. Bolton found that a boiling conc. soln. of **citric acid** decomposes crocoite. J. Spiller said that lead chromate is not precipitated in the presence of **alkali citrates ;** and A. Naumann, that it is insoluble in acetone. J. B. Charcot and P. Yvon said that **saliva** dissolves perceptible amounts of lead chromate. L. Vignon stated that fabrics are usually dyed with lead chromate by passing the material through the aq. soln. of a soluble lead salt and then through a soln. of potassium or sodium chromate. Dyeing also occurs if the material is agitated in a suspension of precipitated lead chromate in water ; equally good results are obtained with silk, wool, or cotton. The lead chromate does not combine chemically with the material dyed. Dyeing also takes place if the lead chromate is suspended in alcohol or benzene, but the resulting colours are not so deep as those obtained when water is the medium of suspension. The reaction was studied by M. A. Iljinsky and V. V. Kozloff.

P. Jannasch observed that natural **silicates** are decomposed when heated strongly with lead chromate. L. Kahlenberg and W. J. Trautmann found that when mixed with silicon and heated by a bunsen burner a sudden reaction occurs with the evolution of heat and light. There is a strong reaction at a "cherry" red-heat and when heated in the electric arc. E. Lay found that **silicon hydrotrinitride** reduces lead chromate at a high temp. M. Lachaud and C. Lepierre found that a soln. of **chromic acid** causes amorphous lead chromate to crystallize, or, according to K. Preis and B. Rayman, to be transformed into lead dichromate ; but, according to W. Autenrieth, a hot, conc. soln. of chromic acid does not dissolve the chromate.

J. Coneybeare said that lead chromate dissolves sparingly in water containing **potassium chromate.** F. Paneth and co-workers, G. M. Schwab and E. Pietsch, and A. Eisner studied the adsorption of radioactive substances by crystals of lead chromate. J. N. Mukherjee and H. L. Ray found that a precipitate of lead chromate in contact with various salts becomes negatively charged in contact with water, this being due, probably, to the adsorption of chromate ions or, alternatively, to the adsorption of hydroxyl ions from the water. The velocity of electrical-osmosis shows that when the lead chromate is in contact with soln. of potassium chromate, iodate, nitrate, iodide, sulphate, and chloride, lead nitrate, barium chloride, and calcium chloride of conc. varying between 0·000067*N* and 0·004*N*, the order of adsorbability of the cations is $Pb^{\cdot\cdot} > Ba^{\cdot\cdot} > Ca^{\cdot\cdot} > K^{\cdot}$, whilst with a constant cation, $K^{\cdot}$, the order of adsorption of the anions is that given above. The constituent ions of a precipitate are very strongly adsorbed by it, those of lead being so largely adsorbed as to reverse the charge at a conc. of 0·00005*N*. These observations cannot be explained on the type of adsorption assumed by F. Paneth; and the suggestion of K. Fajans and K. von Beckerath that there is a parallelism between the intensity of adsorption of the anion and the solubility of the salt of the adsorbed ion with opposite sign in the precipitate is not tenable, since the nitrate is more strongly adsorbed than the iodide or sulphate, whereas the order of increasing solubility of the lead salts is $CrO_4'' < IO_3' < I' < SO_4'' < Cl' < NO_3'$. F. M. Jäger and H. C. Germs studied the binary system: **lead sulphate**—and lead chromate, and obtained the diagram, Fig. 61, which is largely conjectural because of the decomposition at the higher temp. There is a gap in the solid soln. between 30 and 40 per cent. $PbCrO_4$. The mixed crystals have transition points at 934°, 874°, and 748°.

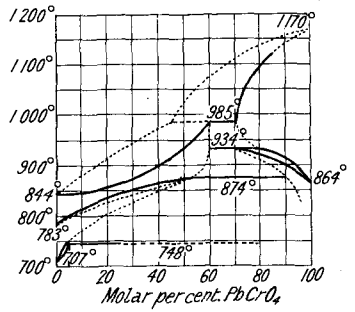



FIG. 61.—Freezing-point Curves of the Binary System: $PbSO_4$–$PbCrO_4$.

A number of **basic lead chromates** has been reported. C. Lückow, and J. J. W. Watson and T. Slater obtained basic salts by the electrolysis of a soln. of

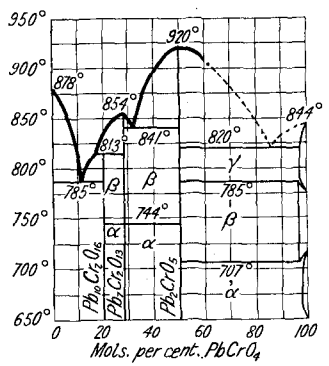



FIG. 62.—Freezing-point Curves of the Binary System: PbO–$PbCrO_4$.

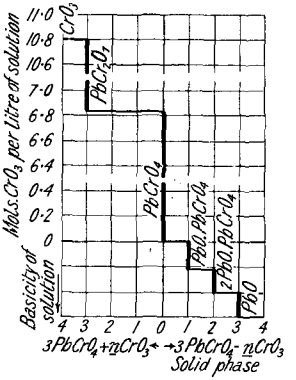
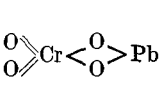



FIG. 63.—Equilibrium Diagram of the Ternary System: PbO–$CrO_3$–$H_2O$ at 25°.

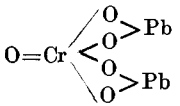
sodium chlorate and chromate with lead electrodes; S. Ganelin, by the action of potassium chromate and magnesia on lead sulphate; A. C. Becquerel, by the action of a zinc plate and water on lead chromate: E. Toelle and M. von Hofe, and J. Kronen, by the action of a paste of lead chromate on lead oxide; H. N. Holmes,

by the action of potassium chromate on soln. of lead salts; and A. Prinvault observed transient violet compounds of apparently high basicity. The equilibrium conditions of fused mixtures of lead oxide and chromate were studied by H. C. Germs, F. M. Jäger and H. C. Germs, J. F. G. Hicks. The f.p. curve of the binary system by F. M. Jäger and H. C. Germs is shown in Fig. 62. The compound $Pb_5CrO_8$, or $Pb_{10}Cr_2O_{16}$, has no real m.p. and is stable only below 815°. The eutectic between $PbCrO_4$ and $Pb_2CrO_5$ occurs at 820°, but this part of the diagram could not be accurately explored because of decomposition. The other basic salt was $Pb_7Cr_2O_{13}$. J. F. G. Hicks obtained $Pb_2CrO_5$, as well as $Pb_4CrO_7$; $Pb_3CrO_6$; and $Pb_3Cr_2O_9$ on his f.p. curve; but the results were obtained by a cruder method. The compounds obtained by the f.p. process, are not necessarily the same as those obtained by wet processes. The results of A. J. Cox's examination of the ternary system: $PbO–CrO_3–H_2O$ at 25°, are summarized in Fig. 63. Here, the basic salts $Pb_3CrO_6$ and $PbCrO_5$ were obtained—*vide supra*, mercury chromates.

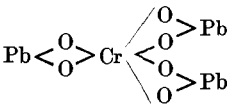
F. M. Jäger and H. C. Germs observed that **lead tetroxychromate,** $5PbO.CrO_3$; $4PbO.PbCrO_4$; $Pb_5CrO_8$; or $Pb_{10}Cr_2O_{16}$, is formed from mixtures of lead chromate with 82·5 to 89 molar per cent. of lead oxide, Fig. 62. The compound is stable below 815°. It decomposes with the evolution of oxygen above its m.p.; and at a temp. exceeding 615°, it decomposes into a liquid and solid $\beta$-$Pb_7Cr_2O_{13}$. J. F. G. Hicks obtained **lead trioxychromate,** $4PbO.CrO_3$; $3PbO.PbCrO_4$; or $Pb_4CrO_7$. from a molten mixture of lead oxide and chromate, but F. M. Jäger and H. C. Germs did not find it—Fig. 62. D. Strömholm added the calculated amount of 0·1*N*-$K_2CrO_4$ to lead hydroxide, and as soon as equilibrium was established; there remained an ochre-yellow mass of small needles of the *monohydrate* of lead trioxychromates, $Pb_4CrO_7.H_2O$. F. M. Jäger and H. C. Germs observed the formation of **lead pentoxybischromate,** $7PbO.2CrO_3$; $5PbO.2PbCrO_4$; or $Pb_7Cr_2O_{13}$, by melting lead chromate with 68 to 82·5 molar per cent. of lead oxide, Fig. 62. It melts at 854° with feeble dissociation. At 774°, there is a reversible transformation with a small thermal change. It forms with lead oxychromate a eutectic at 841° and 68 molar per cent. PbO. They consider that the mineral *melanochroite* from Beresowsk, Urals, is probably this compound—*vide infra*. At 830°, this melanochroite decomposes with the separation of lead. J. F. G. Hicks reported **lead dioxychromate,** $3PbO.CrO_3$; $2PbO.PbCrO_4$; or $Pb_3CrO_6$, to be formed from fused mixtures of lead oxide and chromate, but F. M. Jäger and H. C. Germs did not find it. On the other hand, A. J. Cox observed its formation under the conditions indicated in Fig. 63. This salt can be regarded as a derivative of the hypothetical *orthochromic acid*, $H_6CrO_6$; just as $PbO.PbCrO_4$ can be regarded as a derivative of *parachromic acid*, $H_4CrO_5$.



$PbCrO_4$



$PbO.PbCrO_4$



$2PbO.PbCrO_4$

J. F. G. Hicks, however, does not favour this hypothesis, since it does not explain the constitution of $3PbO.PbCrO_4$.

P. L. Dulong prepared **lead oxychromate,** $2PbO.CrO_3$; $PbO.PbCrO_4$; or $Pb_2CrO_5$, by boiling lead oxide or carbonate with an aq. soln. of potassium chromate. M. Rosenfeld, F. Auerbach and H. Pick, T. Göbel, and J. G. Gentele employed modifications of this process—*cf.* Figs. 62, and 63. L. N. Vauquelin, and M. Faraday exposed to the air a dil. soln. of lead nitrate and potassium chromate in dil. potash-lye, and obtained small crystals which was thought were the normal chromate, but which were shown by F. Wöhler and J. von Liebig to be the oxychromate. C. Reichard obtained the oxychromate by the action of potassium chromate on a soln. of lead sulphate in an aq. soln. of ammonium tartrate; R. Weinland and F. Paul, by the action of potassium chromate on a hot soln. of potassium hydroxy-

chlorate; and A. A. Hayes, by the slow action of carbon dioxide on a soln. of lead oxide and potassium chromate in potash-lye. As the soln. becomes sat. with carbon dioxide, orange-yellow needles of lead oxychromate are formed. F. M. Jäger and H. C. Germs observed that this compound is formed by the fusion of mixtures of lead chromate with 15 to 68 molar per cent. PbO—Fig. 62. J. F. G. Hicks obtained it in a similar manner; and R. F. Marchand, by heating the neutral chromate to redness for some time. A. A. Hayes, J. F. G. Hicks, W. E. Fuss, J. F. G. Hicks and W. A. Craig, F. Wöhler and J. von Liebig, M. Gröger, L. Bourgeois, and M. Lachaud and C. Lepierre obtained it by fusing lead chromate with an alkali nitrate, and leaching out the soluble salt with water. M. Lachaud and C. Lepierre, and J. F. G. Hicks and W. A. Craig, by fusing a mixture of lead oxide and chromate, and sodium chloride. Lead oxychromate is also a product of the hydrolysis of the normal chromate with water or, according to E. F. Anthon, P. Grouvelle, J. F. G. Hicks, C. O. Weber, A. Habich, M. Lachaud and C. Lepierre, with dil. alkali-lye; or, according to F. Auerbach and H. Pick, with 0·1*N*-$Na_2CO_3$. P. L. Dulong, and E. Guignet obtained the same basic salt by boiling lead chromate and carbonate with water; M. Rosenfeld, T. Göbel, P. Grouvelle, and J. Badams, by boiling lead chromate and oxide with water; and J. J. Berzelius, by boiling lead oxide with potassium chromate and water. R. Weinland and R. Stroh prepared the basic chromate **lead dihydroxychromate,** $[Pb(OH)_2]CrO_4$, by double decomposition with lead perchlorate and a soluble chromate. The equilibrium conditions were studied by A. J. Cox—Fig. 63. Analyses were reported by D. Strömholm, M. Gröger, J. F. G. Hicks, M. Lachaud and C. Lepierre, F. Auerbach and H. Pick, J. Badams, etc. The colour of this basic chromate varies from a deep fiery red, cochineal-red, scarlet-red, orange-red, vermilion, etc. Orange-chrome —*vide supra*—is mainly this compound. It may be formed as an amorphous, or eruptic crystalline powder; and the crystals were described by M. Lachaud and C. Lepierre as prismatic needles, which, according to L. Bourgeois, are isomorphous with lanarkite. F. M. Jäger and H. C. Germs said that it furnishes no polymorphic transformation, and that it melts at 920°. The eutectic with lead chromate is at 820° with about 15 molar per cent. of lead oxide. M. Lachaud and C. Lepierre said that it is insoluble in water; and F. Auerbach and H. Pick gave $6\times10^{-35}$ for the solubility product at 18°. M. Lachaud and C. Lepierre found that a litre of 2*N*-KOH at 15° dissolves 10·1 grms.; at 60°, 13·5 grms.; at 80°, 21·9 grms.; and at 102°, 32·1 grms. Dil. acids transform it into lead chromate. Observations on the action of sodium hydrocarbonate soln., by F. Auerbach and H. Pick, are summarized in Fig. 56. J. Badams said that acetic acid extracts half the contained lead oxide.

R. Hermann reported the occurrence of a basic lead chromate in the limestone of Beresowsk, Urals, and he called it **melanochroite**—from μέλας, black; and χρόα, colour—but since the colour of the mineral is red, not black, E. F. Glocker changed the name to *phoenicochroite*—from φοινίκεος, deep-red; and χρόα, colour—and this term was adopted by J. F. L. Hausmann, and J. D. Dana. W. Haidinger's term *phönicite* is more portable, so to speak, but it is too much like phenacite for use. R. Hermann's analysis corresponds with **lead oxybischromate,** $3PbO.2CrO_3$, $PbO.2PbCrO_4$, or $Pb_3Cr_2O_9$. W. E. Dawson gave $4PbO.3CrO_3$ for a variety obtained from Pretoria, Transvaal. Analyses of the artificial chromate in agreement with this were reported by C. Lüdeking, R. Weinland and F. Paul, and M. Lachaud and C. Lepierre. A. Drevermann obtained it together with the normal chromate by the slow mixing by diffusion of soln. of potassium chromate and lead nitrate. R. Weinland and F. Paul obtained it by the action of sodium chromate soln. on a hot soln. of lead hydroxychlorate. A. C. Becquerel obtained it by electrolysis, through a connecting capillary tube, of soln. of potassium dichromate and plumbate; by the electrocapillary action of the same two soln. separated by a collodion or paper partition; by the long continued action of a soln. of potassium chromate on chalk previously boiled with a conc. soln. of lead nitrate; and

by the action for several years of a Pt–Pb-couple on a conc. soln. of chromic chloride and china clay. N. S. Manross, and M. Lachaud and C. Lepierre obtained it by heating at a red-heat a mixture of lead chromate and molten sodium chloride; S. Meunier, by the action of a soln. of potassium dichromate on galena; and C. Lüdeking, by allowing a soln. of lead chromate in conc. potash-lye to stand for some months exposed to air. F. M. Jäger and H. C. Germs observed no sign of this compound in their study of the system $PbO–PbCrO_4$; nor was A. J. Cox more successful in his study of the system: $PbO–CrO_3–H_2O$. J. F. G. Hicks, however, said that he obtained it from fused mixtures of lead oxide and chromate in a molten equimolar mixture of potassium and sodium nitrates. According to R. Hermann, melanochroite is coloured hyacinth-red or cochineal-red, and it becomes lemon-yellow on exposure to air. It occurs in massive, and also in tabular crystals thought to be rhombic. The sp. gr. is 3·0 to 3·5, and the hardness 5·75. A. Drevermann described it as forming rhombic plates coloured like potassium ferricyanide; A. C. Becquerel, as orange-red, doubly refracting needles; and N. S. Manross, as deep red, hexagonal prisms. M. Lachaud and C. Lepierre said that the red, rhombic crystals have a sp. gr. 5·81; A. Drevermann found that the salt does not dissolve as readily as the normal chromate in a soln. of potassium hydroxide. Conc. nitric acid changes it into chrome-yellow.

M. Gröger reported **ammonium lead chromate,** $(NH_4)_2Pb(CrO_4)_2$, by dropping 50 c.c. of a cold, sat. soln. of ammonium chromate into 10 c.c. of a conc. soln. of lead acetate, and allowing the voluminous, yellow, amorphous precipitate to stand for some weeks in contact with the mother-liquor. M. Lachaud and C. Lepierre obtained microscopic, hexagonal plates of **lithium lead chromate,** $Li_2Pb(CrO_4)_2$, by heating freshly precipitated lead chromate with a very conc., neutral soln. of lithium chromate for 8 hrs. in a sealed tube at 140°; and by melting lead chromate with lithium nitrate when some lead oxychromate is formed at the same time. A basic salt could not be prepared. Normal **sodium lead chromate,** $Na_2Pb(CrO_4)_2$, was obtained in a similar way. The yellow prisms or plates are soluble in water. By heating lead chromate, lead oxychromate and sodium chromate in molten sodium nitrate, orange, microscopic prisms of **sodium lead dioxybischromate,** $2PbO.Na_2Pb(CrO_4)_2$, are produced. M. Barre obtained **potassium lead chromate,** $K_2Pb(CrO_4)_2$, from soln. of potassium chromate and lead chromate; L. Bourgeois, and M. Lachaud and C. Lepierre, obtained it by heating lead chromate, or a mixture of lead chromate and potassium chromate in molten potassium nitrate for 3 hrs.; and M. Gröger, by shaking 50 c.c. of an almost sat. soln. of potassium chromate with 10 c.c. of a conc. soln. of potassium acetate—with lead nitrate some hydroxynitrate is formed as well. The yellow, hexagonal plates melt in a crucible over the bunsen flame. The salt is insoluble in water and in alcohol; and with dil. acids, lead chromate is formed. According to M. Barre, the salt is decomposed by water, potassium chromate passing into soln., but with the following proportions of potassium chromate in 100 parts of water, the salt is insoluble at the temp. indicated:

| | 10° | 27·5° | 37·5° | 50° | 70° | 100° |
|---|---|---|---|---|---|---|
| $K_2CrO_4$ . . | 8·950 | 8·077 | 7·629 | 7·150 | 6·145 | 4·940 |

C. Immerwahr said that the electrode potential of lead against lead chromate suspended in $2M$-$K_2CrO_4$ is 0·536 volt. M. Gröger said that the *monohydrate*, $K_2Pb(CrO_4)_2.H_2O$, is formed by the action of lead chromate on potassium acetate soln., or of potassium chromate on lead acetate soln. M. Lachaud and C. Lepierre obtained **potassium lead dioxychromate,** $2PbO.K_2Pb(CrO_4)_2$, in orange prisms by the method used for the sodium salt. M. Lachaud and C. Lepierre also prepared **barium, strontium, and calcium lead chromates** by the method used for the alkali salts. For **copper lead chromate,** *vide infra*, vauquelinite. A. Breithaupt described a mineral from Berezoff, Urals, as occurring in orange-yellow crystals—possibly **zinc lead chromate.** The mineral was called **jossoite.** Its sp. gr. is 5·2; and its hardness 3.

S. H. C. Briggs [26] heated 3·5 grms. of antimony oxychloride, $2SbOCl.Sb_2O_3$, with 6 grms. of chromic trioxide and 6 c.c. of water in a sealed tube for 4 hrs. at 200°. The tube contained a straw-yellow sublimate, and an orange-yellow deposit in spherical, crystalline aggregates, insoluble in water, and slowly soluble in nitric acid—*vide supra*, antimony chromite. The composition approximated *antimony tetroxybischromate*, $3SbO_2.2CrO_3$, or $Sb_3O_4(CrO_4)_2$. Although normal **bismuth chromate,** $Bi_2(CrO_4)_3$, has not been prepared, K. Preis and B. Rayman obtained what they regarded as **potassium bismuth chromate,** $4K_2CrO_4.Bi_2(CrO_4)_3$, by mixing a soln. of 2 mols of bismuth nitrate with a soln. of 9 mols of potassium chromate. The precipitate is non-crystalline. J. Milbauer obtained only a 6·3 per cent. conversion to chromate when a mixture of bismuth oxide or carbonate and chromic oxide was heated to 480° in oxygen at 12 atm. press. A number of basic salts has been reported, with $Bi_2O_3 : CrO_3 : H_2O = 3 : 1 : 0$; $3 : 2 : 0$; $1 : 1 : 0$; $1 : 2 : 1$; $5 : 11 : 6$; and $3 : 7 : 0$. Of these, A. J. Cox recognized only the $1 : 2 : 1$-compound—the $1 : 4 : 1$-compound may be a basic dichromate. The $5 : 11 : 6$-compound, reported by M. M. P. Muir to be formed by the protracted boiling of the $1 : 4 : 1$-compound with dil. nitric acid, is considered by A. J. Cox to be an impure $1 : 2 : 1$-compound; and a similar remark applies to the $3 : 7 : 0$-compound reported by M. M. P. Muir to be formed by heating the $1 : 4 : 1$-compound with conc. nitric acid. The other basic salts are supposed to be impure $1 : 2 : 1$ or $1 : 4 : 1$-compounds or mixtures of these. The results of A. J. Cox's examination of the ternary system: $Bi_2O_3$–$CrO_3$–$H_2O$ at 25° are summarized in Fig. 64. If the soln. at 25° has a smaller conc. than 7·80 mols of $CrO_3$ per litre, the $1 : 4 : 1$-compound is hydrolyzed and it passes into the $1 : 2 : 1$-compound, which is stable even when the soln. is almost pure water. S. H. C. Briggs did not succeed in making a bismuth chromate—*vide supra*, bismuth chromite.

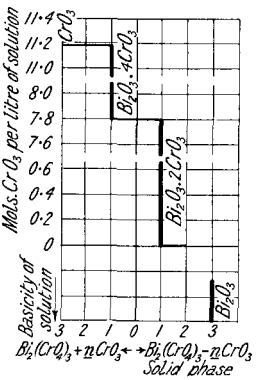



FIG. 64.—Equilibrium Diagram of the Ternary System: $Bi_2O_3$–$CrO_3$–$H_2O$ at 25°.

W. Schmid reported the $3 : 1 : 0$-compound or $3Bi_2O_3.CrO_3$, which may be **bismuthyl orthochromate,** $(BiO)_6CrO_6$. It is said to be formed by boiling bismuthyl hydroxide with a conc. soln. of potassium chromate. The heavy, pale orange powder is washed with boiling water. It can be heated to redness without decomposition. J. Löwe prepared the $3 : 2 : 0$-compound—possibly **bismuthyl paradichromate,** $(BiO)_3{\equiv}CrO{-}O{-}CrO{\equiv}(BiO)_3$—by pouring a soln. of bismuth nitrate, containing as little free nitric acid as possible, into an excess of a soln. of potassium chromate, and washing the product with hot water. W. Schmid obtained it by heating the $1 : 2 : 1$-compound with molten potassium nitrate, and leaching the soluble salts from the cold product with water; and M. M. P. Muir, by boiling the $5 : 11 : 6$- or the $3 : 7 : 0$-compound with potash-lye. A. J. Cox regarded this product as a mixture of bismuth oxide and the $1 : 2 : 1$-compound. J. Löwe said that the lemon-yellow, micro-crystalline powder contains only one per cent. of water when dried at 110°. It can be heated to redness without melting or without decomposition. It is insoluble in cold or hot water; it is freely soluble in an excess of dil. hydrochloric or nitric acid, but if the acid be not in excess, the $1 : 2 : 1$-compound is formed. When boiled with dil. soda-lye, it forms a bright red basic salt. "Bismuth chromate," said A. Naumann, "is insoluble in acetone."

M. M. P. Muir reported the $1 : 1 : 0$-compound, **bismuthyl chromate,** $Bi_2O_3.CrO_3$, or $(BiO)_2CrO_4$, to be formed by treating a soln. of bismuth nitrate with an excess of potassium chromate or dichromate, and, after the addition of a few drops of nitric acid, boiling the mixture for a few hours until it is transformed into a red powder. The product is washed with hot water, and dried at 100°. It is also obtained by

boiling the 1 : 2 : 1-compound with a soln. of potassium dichromate and hydroxide. The vermilion-coloured powder consists of microscopic needles. It does not decompose when heated in a crucible over the bunsen-flame, but when strongly heated it becomes dark brown ; it is insoluble in water, soluble in dil. hydrochloric acid, but not so soluble in dil. nitric or sulphuric acid. Boiling soda-lye converts part of it into the 3 : 1 : 0-compound, and part is dissolved.

J. Löwe poured a nearly neutral soln. of bismuth nitrate into an excess of a warm soln. of potassium dichromate and boiled the mixture for some time. The product, washed with water and dried at 140°, consisted of $Bi_2O_3.2CrO_3$, or $Bi_2O_3.2CrO_3$, that is, *bismuthyl dichromate*, $(BiO)_2Cr_2O_7$, or **bismuth hydroxychromate,** $Bi(OH)CrO_4$. M. M. P. Muir, W. Schmid, and K. Preis and B. Rayman also prepared this salt. R. W. Pearson obtained a product by a similar process, but regarded it as the 1 : 1 : 0-compound. F. Nolle also prepared a similar salt. A. J. Cox showed that this compound is produced by the hydrolysis of the 1 : 4 : 0-compound—Fig. 64. At 25°, the salt is stable in the presence of water containing not less than 0·00001 mol of chromic acid per litre. J. Löwe obtained it by the action of mineral acids on the 1 : 1 : 0-compound ; W. Schmid, by boiling bismuthyl hydroxide with an excess of a soln. of chromic acid ; and M. M. P. Muir, by the action of dil. nitric acid on the 1 : 4 : 1-compound. J. Löwe, W. Schmid, and A. J. Cox supposed the salt to be anhydrous ; and M. M. P. Muir, hydrated. The anhydrous salt consists of minute, orange-yellow scales, which decompose at a red-heat ; and are insoluble in hot or cold water, but soluble in dil. mineral acids.

M. M. P. Muir prepared the 1 : 4 : 1 compound—*bismuth hydroxydichromate,* $Bi_2O_3.4CrO_3.H_2O$, or else **bismuthyl quaterochromate,** $BiO.O.CrO_2.O.CrO_2.O.CrO_2.O.CrO_2.O.BiO$, without combined water—by boiling the 1 : 1 : 0-compound with a little conc. nitric acid. A. J. Cox obtained it by the action of chromic acid on bismuth oxide provided the soln. contains at least 7·8 mols of $CrO_3$ per litre at 25°—Fig. 64. The salt is washed with a similar soln. of chromic acid. The salt prepared by A. J. Cox was not hydrated ; M. M. P. Muir's product was said to be the monohydrate when dried at 100° ; but A. J. Cox said that it was not completely dried. M. M. P. Muir found that the water is expelled at 200°–250°. The small ruby-red crystals are monoclinic prisms which decompose when strongly heated, forming a reddish vapour and a green residue. It is insoluble in hot and cold water ; but it dissolves freely in mineral acids ; with conc. hydrochloric acid, chlorine is evolved. It forms a pale orange product when boiled for a long time with dil. nitric acid.

The **vanadium chromates** have been discussed in connection with the chromium vanadates. According to C. W. Blomstrand,[27] an aq. soln. of columbium oxychloride gives a yellow, granular precipitate of **columbium chromate** when it is treated with potassium chromate.

The so-called **chromium chromates** have been discussed in connection with the oxides $Cr_5O_9$, or $2Cr_2O_3.CrO_3$ ; $Cr_8O_{15}$, or $3Cr_2O_3.2CrO_3$ ; $CrO_2$, or $Cr_2O_3.CrO_3$ ; $Cr_4O_9$, or $Cr_2O_3.2CrO_3$ ; $Cr_5O_{12}$, or $Cr_2O_3.3CrO_3$ ; and $Cr_6O_{12}$, or $Cr_2O_3.4CrO_3$. H. J. S. King prepared **chromic hydroxypentamminochromate,** $[Cr(NH_3)_5(OH)]CrO_4$, by the action of the chloride of the base in ammoniacal soln. on ammonium chromate. O. T. Christensen[28] prepared **chromic nitritopentamminochromate,** $[Cr(NH_3)_5(NO_2)]CrO_4$, by treating the corresponding chloride with a cold, sat. soln. of potassium chromate. The salt forms small, yellow crystals, sparingly soluble in water ; and they explode like gunpowder when heated. A. Hiendlmayr prepared **chromic fluopentamminochromate,** $[Cr(NH_3)_5F]CrO_4$, by the action of potassium chromate on a soln. of the chloride of the series. S. M. Jörgensen prepared **chromic chloropentamminochromate,** $[Cr(NH_3)_5Cl]CrO_4$, by treating the corresponding chloride or nitrate with potassium chromate, and, after filtration, washing the product with cold water. The microscopic, rhombic plates are soluble in water. P. T. Cleve obtained **chromic aquo-**

**chlorotetramminochromate,** $[Cr(NH_3)_4)H_2O)Cl]CrO_4$, from a soln. of the corresponding chloride by the addition of potassium chromate. The brownish-black powder decomposes when heated. S. M. Jörgensen obtained **chromic bromopentamminochromate,** $[Cr(NH_3)_5Br]CrO_4$, from a cold sat. soln. of the nitrate by the addition of *N*-$K_2CrO_4$. The brownish-red product forms the chloride when treated with hydrochloric acid. He also prepared **chromic oxyaquotrihydroxyhexamminochromate,** $[Cr_2(O_4H_5)(NH_3)_6]_2(CrO_4)_3.5H_2O$, or

$$\begin{bmatrix} (NH_3)_2 & & (NH_3)_4 \\ (H_2O)\ Cr{-}O{-}Cr & & (OH) \\ (HO)_2 & & \end{bmatrix}_2 (CrO_4)_3,5H_2O$$

by the action of potassium chromate in excess on a soln. of the chloride. The microscopic, reddish-brown, rhombic plates are sparingly soluble in water. P. Pfeiffer and W. Vorster prepared **chromic hexaethylenediaminohexahydroxychromate,** $[Cr_4(OH)_6(en)_6](CrO_4)_3.5H_2O$, from a soln. of the chloride and a conc. soln. of potassium chromate. The brownish-red compound is decomposed by a prolonged boiling with water. W. J. Sell prepared **chromic hexacarbamidochromate,** $[Cr(CON_2H_4)_6](CrO_4)_3.4H_2O$.

J. J. Berzelius[29] obtained a basic **molybdenum chromate** by adding potassium chromate to a soln. of molybdenum chloride; and another basic salt as a precipitate by adding ammonia to a soln. of the dichromate. The pale yellow soln. when spontaneously evaporated furnishes white or yellowish-white acicular or scaly crystals which are efflorescent. A. Atterberg prepared **molybdous tetrabromochromate,** $[Mo_3Br_4]CrO_4$. If a soln. of molybdous tetrabromodihydroxide in alkali-lye be treated with potassium dichromate, no precipitate is formed; but if an acid, say acetic acid, be also added, the soln. becomes dark red, and a dark purple-brown powder is precipitated. The compound decomposes when heated. It is insoluble in dil. acids, but soluble in hot, conc. hydrochloric acid. It is decomposed by alkali-lye; and it is insoluble or sparingly soluble in soln. of alkali chromates. For **tungsten chromates,** see chromium tungstates.

According to H. Moser, and J. J. Berzelius, potassium chromate gives an ochre-yellow precipitate with uranyl nitrate; and C. F. Rammelsberg obtained a precipitate with uranium tetrachloride and potassium chromate—*vide supra*, uranium chromite; while J. F. John observed that a soln. of yellow uranic carbonate in chromic acid deposits red, cubic and dendritic crystals, which fuse with partial decomposition at a red-heat. According to N. A. Orloff, a sat. soln. of uranium trioxide in chromic acid, yields, on evaporation, yellow needles of normal **uranyl chromate,** $(UO_2)CrO_4.3H_2O$. At 15°, 100 parts of water dissolve 7·52 parts of the *trihydrate* forming a pure yellow soln., which, on evaporation at 100°, gives an amorphous, brown mass, soluble in water to a brown soln. Uranyl chromate dissolves slowly in alcohol at the ordinary temp.; this soln. decomposes on boiling, also when exposed to the action of sunlight, with the separation of a brown precipitate. The filtrate from this precipitate when evaporated to dryness yields an amorphous, brown mass, partially soluble in water; it probably consists of a mixture of uranyl chromate and chromous uranate. According to J. Formanek, the *henahydrate*, $(UO_2)CrO_4.11H_2O$, obtained by dissolving the hydroxide in an aq. soln. of chromic acid and concentrating the filtered soln. on the water-bath, crystallizes from boiling water in yellow needles, effloresces on exposure to the air, and loses the whole of its water at 200°; only silver, lead, mercurous, and bismuth salts produce precipitates in its aq. soln. In precipitating chromic acid as mercurous chromate, in presence of uranium salts, the mercurous nitrate employed must be free from oxides of nitrogen, and the soln. must be slightly acidic; otherwise some of the uranium salt is also precipitated. J. Aloy gave −6·3 Cals. for the heat of soln. of a mol of this salt in 1000–2500 mols of water at 18°–20°. According to N. A. Orloff, when potassium chromate is added to an aq. soln. of uranyl chromate, the basic salt, yellow **uranyl oxybischromate,** $UO_3.2UO_2CrO_4.8H_2O$, or

$(UO_2)_3O(CrO_4)_2.8H_2O$, is formed; and if uranyl acetate is similarly treated, **uranyl oxychromate,** $UO_3.UO_2CrO_4.6H_2O$, or $(UO_2)_2O(CrO_4).6H_2O$, is formed. He added that the formation of the basic salts indicates that in soln. uranyl chromate behaves like a mixture of uranic and chromic acids. S. H. C. Briggs obtained a complex, $2UO_3.3CrO_3.2Py$, with pyridine.

J. Formanek observed that yellow plates of **ammonium uranyl chromate,** $(NH_4)_2CrO_4.2(UO_2)CrO_4.6H_2O$, are produced by mixing a soln. of a mol of uranyl nitrate with a soln. of a mol of ammonium chromate, and evaporating the liquor over sulphuric acid; the same salt is obtained by treating ammonium uranate with a warm, conc. soln. of chromic acid, and evaporating the filtered liquid over sulphuric acid. The yellow, monoclinic crystals of the *hexahydrate* have the axial ratios $a:b:c=0{\cdot}8016:1:1{\cdot}0196$, and $\beta=72°\ 31'$. The salt is partially decomposed by boiling water. In some cases, probably owing to a variation of temp., orange-red crystals of a *trihydrate* were formed. J. Formanek obtained **potassium uranyl chromate,** $K_2CrO_4.2UO_2CrO_4.6H_2O$, by a process analogous to that employed for the ammonium salt. The axial ratios of the yellow, monoclinic plates or prisms were $a:b:c=0{\cdot}7566:1:0{\cdot}9714$, and $\beta=107°\ 22'$. The salt is soluble in acidulated water, and it is decomposed by boiling water. J. Wiesner reported a number of complex potassium salts are formed by precipitation from mixtures of uranyl nitrate and potassium chromate, *viz.*, $K_4(UO_2)_3(CrO_4)_5.7H_2O$; $K_6(UO_2)_4(CrO_4)_7.7H_2O$; $K_2(UO_2).(CrO_4)_2.H_2O$; and $K_2Cr_2O_7.3(UO_2)CrO_4.14H_2O$. J. Formanek, H. Bürger, and E. Rimbach obtained yellow crystals of **sodium uranyl chromate,** $Na_2CrO_4.2UO_2CrO_4.10H_2O$, by a process analogous to that employed for the ammonium salt. The salt is freely soluble in water, without decomposition. J. Formanek obtained **silver uranyl chromate** as a vermilion precipitate by treating a soln. of uranyl chromate with silver nitrate. Unlike J. Formanek, B. Szilard was unable to detect any decomposition of silver uranyl chromate in light even after several days' exposure. J. Formanek prepared **mercurous uranyl chromate** in a similar manner; so also **lead uranyl chromate**; and **bismuth uranyl chromate.**

According to J. F. John,[30] an aq. soln. of chromic acid slowly dissolves manganese with the evolution of hydrogen; manganous oxide and carbonate are also dissolved by the acid forming, presumably, soln. of **manganous chromate.** The soln. has an acidic reaction and a pungent, metallic taste, and after repeated evaporation it deposits nearly all the manganese in a higher state of oxidation. T. Thomson said that potassium chromate or dichromate does not give a precipitate with manganous salts immediately, but after some time, especially with the chromate, a brownish-black precipitate is produced. According to U. Antony and U. Paoli, if excess of alkali hydroxide be added to a soln. containing a chromium and a manganese salt in the proportion Mn : 8Cr(O=16), no precipitate is obtained, but the liquid is coloured emerald green and must be regarded as a colloidal soln. of the hydroxides of chromium and manganese, since this behaviour is exhibited only when the salts are present in exactly the above ratio. Chromium being tervalent and having both an acid and basic function, whilst manganese is bivalent and decidedly metallic in its properties, it is inferred that they exist in this soln. in the form of a salt, an electrolyte, which must be either a manganous chromite or polychromite. When this liquid is exposed to the air, or, better, when oxygen is passed through it, it quickly turns brown but remains free from precipitate. The element undergoing the oxidation is the manganese which becomes quadrivalent; the *rôles* of the two elements thus become interchanged and a more or less basic chromium manganite is formed. The chromium hydroxide now begins to undergo oxidation and the amount of chromate formed in the soln. increases until about 60 per cent. of the chromium has been converted. Continued action of oxygen has now no further effect on the liquid which, after a time, deposits a dark precipitate of constant composition, the proportion Mn : Cr having the value 1 : 3; when this compound is treated with cold dil. sulphuric acid, the chromium dissolves as sulphate whilst the manganese remains in soln. as the hydrate of manganese dioxide.

If now to this liquid is added an alkaline soln. of chromium hydroxide, the latter undergoes immediate and complete oxidation. U. Antony and U. Paoli also measured the speed of the oxidation. R. Warington observed that manganous salts are coloured yellowish-brown by potassium chromate, and in time a dark brown precipitate is formed; which, with dil. soln., may be crystalline **manganous oxychromate,** $MnO.MnCrO_4.2H_2O$, in agreement with the analyses of R. Warington, and H. Reinsch. C. Freese obtained a similar salt from a boiling soln. of manganous sulphate and potassium chromate; and A. J. Fairrie, using manganous chloride, obtained what he regarded as $3Mn_2O_3.Cr_2O_3.3CrO_3.6H_2O$. E. Schulze was unable to obtain a manganous chromate from a cold soln. of manganous carbonate and chromic acid. C. Freese said that the oxychromate loses half its water at 180° and the remainder at 300°; P. Grouvelle, that the salt is slightly soluble in water; and R. Warington, that with potash-lye it furnishes potassium chromate; with hydrochloric acid it gives chlorine; and dissolves in sulphuric or nitric acid forming an orange-yellow liquid. E. Donath described the use of manganese chromate as a pigment *chrome-brown*. C. Hensgen prepared **ammonium manganous chromate,** $(NH_4)_2CrO_4.2MnCrO_4.4H_2O$, as a precipitate from a mixed soln. of manganous and ammonium sulphates. It can be crystallized from a soln. of chromic acid. The bluish-black crystals resemble iodine. It decomposes at 200°, and if the salt be rapidly heated, a slight explosion occurs. The corresponding **ammonium manganous trischromate,** $K_2CrO_4.2MnCrO_4.2H_2O$, was obtained in a similar way, and by varying the proportions of the component salts used in the preparation, intermediate compounds are formed. M. Gröger obtained **potassium manganous bischromate,** $K_2CrO_4.MnCrO_4.2H_2O$, from $4N\text{-}K_2CrO_4$ mixed with an equal vol. of $N\text{-}MnCl_2$. F. Breinl and J. Klaudy supposed the salt to be monohydrated. According to M. Gröger, the salt is decomposed by water, with the separation of a brown precipitate. It gives an orange-red soln. with sulphuric acid. No definite compound was obtained by using a greater excess of the chromate soln., and with boiling soln. chromium manganite is formed.

It is scarcely to be expected that **ferrous chromate** could be prepared in aq. soln. because of the strongly oxidizing properties of the chromates and chromic acid; L. N. Vauquelin [31] obtained a yellowish-brown precipitate on adding potassium chromate to a soln. of ferrous sulphate. The precipitate gave up no chromic acid to alkali-lye, and formed a green soln. with nitric acid. C. Lepierre found that the product of the action is a basic complex ferric salt—*vide infra*. Neither A. Maus, nor C. W. Eliot and F. H. Storer, were able to prepare normal **ferric chromate.** According to A. Maus, if a soln. of a ferric salt be treated with alkali chromate, a brown powder is formed which is resolved by water into soluble chromic acid, and insoluble ferric oxide. A brown soln. is obtained when hydrated ferric oxide is digested with chromic acid. The soln. is not rendered turbid by dilution with water, or by boiling; and, on evaporation, it yields a brown mass soluble in water and in alcohol. L. A. Wels found the magnetic susceptibility of **potassium ferric chromate,** $K[Fe(CrO_4)_2].2H_2O$, to be $39{\cdot}44\times10^{-6}$ mass unit. The brown product obtained by the action of potassium chromate on a soln. of a ferric salt was found by V. Kletzinsky, and C. W. Eliot and F. H. Storer to have the composition of **ferryl chromate,** $(FeO)_2CrO_4$. L. Blanc also prepared the basic chromate. S. H. C. Briggs obtained ferric oxybischromate, $2Fe_2O_3.4CrO_3.H_2O$, or $(FeCrO_4)_2O.\frac{1}{2}H_2O$, by treating 5 grms. of ferric chloride as in the case of the aluminium salt. The shining black crystals were mixed with a highly coloured, more basic substance. According to C. Hensgen, **ammonium ferric chromate,** $(NH_4)_2CrO_4.Fe_2(CrO_4)_3.4H_2O$, is obtained when the precipitate, produced by mixing conc. soln. of ammonium chromate and ferric chloride, is dissolved in hydrochloric acid, and the soln. slowly evaporated. The dark red, leafy, crystalline mass is rapidly washed with cold water, or with alcohol and ether. It decomposes when heated, or when left in contact with water. C. Lepierre obtained the same salt in red crystals by evaporating a cold soln. of ferric chloride and

ammonium dichromate. C. Hensgen obtained **potassium ferric chromate,** $K_2CrO_4.Fe_2(CrO_4)_3.4H_2O$, by a process analogous to that used for the ammonium salt; it is decomposed slowly by water. According to R. Weinland and E. Mergenthaler, when a mixed soln. of ferric nitrate, chromic acid, and ammonia is heated on a water-bath, carmine red, insoluble ammonium ferric chromate, $NH_4[Fe(CrO_4)_2]$, separates; and likewise, under analogous conditions, potassium ferric chromate, $K[Fe(CrO_4)_2].2H_2O$, as a sparingly soluble, dark orange-red, microcrystalline powder. With pyridine under similar conditions, there is formed **pyridine ferric chromate,**

$$\left[Fe(CrO_4)_6\right]^{H_6}_{H_3(C_5H_5N)_3}$$

C. Lepierre found that C. Hensgen's salt is produced by the action of ferric chloride with a large excess of potassium dichromate; if ferric chloride be in excess, potassium chlorochromate is one of the products; if neither salt is in excess, ruby-red crystals of the basic salt *potassium ferric oxyseptieschromate,* $2K_2CrO_4.Fe_2(CrO_4)_3.FeO(CrO_4)_2.7H_2O$, are formed; and if the one soln. is allowed to diffuse into the other, anhydrous crystals of *potassium ferric trioxysexieschromate,* $3K_2CrO_4.Fe_2O_3.Fe_2(CrO_4)_3$, are produced. A sat. soln. of potassium chromate when added to an excess of a sat. soln. of ferric chloride yields ruby-red hexagonal crystals of *potassium ferric dioxyundecieschromate,* $4K_2CrO_4.2Fe_2(CrO_4)_3.(FeO)_2CrO_4$; with an excess of chromate, an orange-yellow precipitate of *potassium ferric trioxynovieschromate,* $6K_2CrO_4.Fe_2O_3.Fe_2(CrO_4)_3.nH_2O$, is formed—*hexahydrate,* if washed with alcohol, and the *decahydrate* if washed with water; with only a slight excess of ferric salt, *potassium ferric pentoxydecieschromate,* $6K_2CrO_4.Fe_2O_3(FeO)_2CrO_4.Fe_2(CrO_4)_3$. In all cases, in hot soln., the products are mixtures. If a soln. of 6 mols of ferrous sulphate and 2 mols of potassium chromate be allowed to react at 0°, *potassium ferric enneadecaoxybischromate,* $3K_2O.6Fe_2O_3.2CrO_3$, is formed. It is washed with water, alcohol, and ether at 0°; when moist, it is brown, and when dried, black. After drying in the air, it retains about 30 per cent. of water. The action of ferrous sulphate on potassium chromate at higher temp. yields only basic ferric sulphates. The action of excess of potassium chromate on ferrous sulphate yields a yellowish-brown, micro-crystalline precipitate of *potassium ferric enneaoxyquaterchromate,* $4K_2CrO_4.3Fe_2O_3$, which retains 22·7 per cent. of water when dried in air. If ammonium ferrous sulphate be employed, the precipitate is *potassium ferric pentadecaoxydecieschromate,* $7K_2CrO_4.Fe_2(CrO_4)_3.5Fe_2O_3$. If ferric chloride be employed with sodium chromate, *sodium ferric oxyquinquieschromate,* $4Na_2CrO_4.6Fe_2O_3.(FeO)_2CrO_4$, is formed; and with ammonium chromate, *ammonium ferric pentadecaoxysexieschromate,* $6(NH_4)_2CrO_4.5Fe_2O_3$. If ammonium and sodium dichromates are employed, immediate oxidation occurs without forming basic chromates. It is not to be supposed that these basic salts are all chemical individuals.

Potassium chromate with soln. of cobalt salts gives a reddish-brown precipitate which is probably a basic salt. F. J. Malaguti and M. Sarzeau [32] represented it as **cobaltous dioxychromate,** $2CoO.CoCrO_4.4H_2O$, or $3CoO.CrO_3.4H_2O$. S. H. C. Briggs obtained **cobaltous chromate,** $CoCrO_4$, by heating a soln. of the carbonate in chromic acid in a sealed tube at 260° for several hrs. The greyish-black crystals are readily soluble in dil. nitric acid. The *dihydrate,* $CoCrO_4.2H_2O$, is obtained in bronze coloured prisms or leaflets, when soln. of cobalt acetate and potassium chromate are mixed. The salt is always contaminated with some double chromate. F. de Boer studied the X-ray spectrum. N. Parravano and A. Pasta obtained yellow needles of *cobaltous bisethylenediaminochromate,* $CoCrO_4.2C_2H_4(NH_2)_2$. C. Freese said that **cobaltous oxychromate,** $CrO.CoCrO_4.2H_2O$, appears as a reddish-brown precipitate when boiling soln. of a cobaltous salt and potassium chromate are mixed. One mol. of water is expelled at about 220°, and the other at about 300°. The dehydrated salt slowly takes up water again from moisture. M. Gröger dissolved cobalt carbonate in the cold soln. of an eq. amount of *N*-$CrO_3$. The filtrate is evaporated, and when the residue is taken up with water there remains the brownish-black *monohydrate* of cobaltous oxychromate. F. J. Malaguti and M. Sarzeau found that when the dioxychromate is treated with ammonia it forms orange-yellow needles, and an amorphous, ruby-red product.

O. W. Gibbs and F. A. Genth, and C. D. Braun treated cobaltic hexamminonitrate with potassium chromate and obtained a yellow precipitate of **cobaltic hexamminochromate,** $[Co(NH_3)_6]_2(CrO_4)_3.5H_2O$. O. W. Gibbs and F. A. Genth,

C. D. Braun, and T. Klobb also prepared **cobaltic hexamminochlorochromate,** $[Co(NH_3)_6]Cl(CrO_4)$ with $1\frac{2}{3}$ and with 3 mols. of water. G. Vortmann treated an aq. soln. of cobaltic chloroaquotetramminochloride with potassium dichromate and obtained **cobaltic octamminochromate,** $Co_2(NH_5)_8(CrO_4)_3.4H_2O$. The brown precipitate furnishes bronze brown plates of the *tetrahydrate* when recrystallized from dil. acetic acid. If potassium chromate be used as precipitant, the olive-green *decahydrate* is formed. According to S. H. C. Briggs, if a cobaltic diaquotetrammino-salt is added to a large excess of neutral sodium chromate, dark chocolate-brown cobaltic octamminochromate, $Co_2(CrO_4)_3.8NH_3.2\frac{1}{2}H_2O$, is formed, and this furnishes the monohydrate, if kept in vacuo. A. Hiendlmayr prepared **cobaltic fluopentamminochromate,** $[Co(NH_3)_5F]CrO_4$, by the action of potassium chromate on a soln. of the fluoride of the series. O. W. Gibbs prepared **cobaltic nitritopentamminochromate,** $[Co(NH_3)_5NO_2]CrO_4.H_2O$, as a yellow precipitate by adding potassium chromate to the corresponding nitrate. J. N. Brönsted and A. Petersen found its molar solubility at 20° to be $S=0{\cdot}000258$ and in the presence of various salts of molar conc. $C$,

| | $C$ | 0·02 | 0·05 | 0·10 | 0·20 | 0·50 | 1·0 |
|---|---|---|---|---|---|---|---|
| $S$ | H.COOK | $0{\cdot}0_3361$ | $0{\cdot}0_3481$ | $0{\cdot}0_3636$ | $0{\cdot}0_3816$ | $0{\cdot}0_21212$ | $0{\cdot}0_21787$ |
| | H.COONa | $0{\cdot}0_3323$ | $0{\cdot}0_3410$ | $0{\cdot}0_3558$ | $0{\cdot}0_3746$ | $0{\cdot}0_21131$ | $0{\cdot}0_21729$ |
| | NaCl | — | $0{\cdot}0_3425$ | $0{\cdot}0_3565$ | $0{\cdot}0_3785$ | — | — |
| | KCl | $0{\cdot}0_3371$ | $0{\cdot}0_3520$ | $0{\cdot}0_3690$ | $0{\cdot}0_3887$ | — | — |
| | $KClO_3$ | $0{\cdot}0_3332$ | $0{\cdot}0_3421$ | $0{\cdot}0_3570$ | — | — | — |
| | $NaClO_3$ | $0{\cdot}0_3318$ | $0{\cdot}0_3417$ | $0{\cdot}0_3561$ | — | — | — |
| | $KNO_3$ | $0{\cdot}0_3345$ | $0{\cdot}0_3444$ | $0{\cdot}0_3588$ | — | — | — |
| | $NaNO_3$ | $0{\cdot}0_3344$ | $0{\cdot}0_3442$ | $0{\cdot}0_3577$ | — | — | — |
| | $MgSO_4$ | $0{\cdot}0_362$ | $0{\cdot}0_3908$ | $0{\cdot}0_21237$ | $0{\cdot}0_21804$ | — | $0{\cdot}0_25120$ |

They also studied *cobaltic isothiocyanatopentamminochromate,* $[Co(NH_3)_5SCy]CrO_4$; and *cobaltic tetrathiocyanatodiamminochromates;* P. R. Ray prepared **cobaltic thiosulphatopentamminochromate,** $[Co(NH_3)_5(S_2O_3)]_2CrO_4$, by adding potassium chromate to the corresponding chloride. S. M. Jörgensen obtained, in an analogous manner, yellow, microscopic needles of **cobaltic cis-dinitritotetramminochromate,** $[Co(NH_3)_4(NO_2)_2]_2CrO_4$, and O. W. Gibbs, **cobaltic trans-dinitritotetramminochromate.** S. M. Jörgensen likewise obtained **cobaltic nitratopentamminochromate,** $[Co(NH_3)_5NO_3]CrO_4$, in ochre-yellow or brick-red octahedral crystals; also brick-red, microscopic crystals of **cobaltic chloropentamminochromate,** $[Co(NH_3)_5Cl]CrO_4$; and likewise greyish-brown, rosetted needles of **cobaltic chloroaquotetramminochromate,** $[Co(NH_3)_4(H_2O)Cl]CrO_4$; and brown, six-rayed aggregates of **cobaltic bromopentamminochromate,** $[Co(NH_3)_5Br]CrO_4$.

S. H. C. Briggs added a soln. of a cobaltic diaquotetrammino-salt to a large excess of an alkali chromate and obtained a series of alkali bischromatotetramminocobaltiates, $M'[Co(CrO_4)_2(NH_3)_4]$. A green form corresponds with the trans-configuration, and a brown form with the cis-configuration of the chromate radicles. The formation of the brown form is favoured by the presence of a large proportion of dichromate in the soln. The salts obtained were **lithium cis-bischromatotetramminocobaltiate,** $Li[Co(CrO_4)_2(NH_3)_4].1\frac{1}{2}H_2O$; **sodium trans-bischromatotetramminocobaltiate,** $Na[Co(CrO_4)_2(NH_3)_4]$, as a green, microcrystalline powder; and the corresponding **sodium cis-bischromatocobaltiate,** $Na[Co(CrO_4)_2.(NH_3)_4].H_2O$, in greenish-brown crystals; and **potassium trans-bischromatotetramminocobaltiate,** $K[Co(CrO_4)_2(NH_3)_4]$. If magnesium chromate be employed, **magnesium cis-bischromatotetramminocobaltiate,** $Mg[Co(CrO_4)_2(NH_3)_4]_2.2H_2O$, is formed in brown crystals, and also **magnesium trans-bischromatotetramminocobaltiate,** $Mg[Co(NH_3)_4(CrO_4)_2]_2.8H_2O$, which, when dehydrated in vacuo over sulphuric acid, gives the *hexahydrate.* The *octohydrate* is thought to be $Mg[Co(NH_3)_4(CrO_4)_2(H_2O)_2]_2.4H_2O$, in which the co-ordination number of the cobalt atom is eight. If a cobaltic diaquotetrammino-salt be added to a large excess of neutral ammonium chromate, dark reddish-brown crystals of **ammonium chromatopentamminobischromate,**

$(NH_4)_2[Co(CrO_4)(NH_3)_5](CrO_4)_2$, are formed. With sodium chromate, the octammine is formed as indicated above.

M. Gröger prepared ammonium **cobaltous oxyquaterochromate,** $(NH_4)_2CrO_4.CoO.3CoCrO_4.3H_2O$, by the action of 2 vols. of *N*-$CoCl_2$ on one vol. of *N*-$(NH_4)_2CrO_4$. On allowing the precipitate to stand in contact with the mother-liquor for some time, dark brownish-red microscopic crystals are formed. The composition is different if other proportions of the constituent salt soln. are mixed. S. H. C. Briggs prepared **ammonium cobaltous chromate,** $(NH_4)_2CrO_4.CoCrO_4.6H_2O$, in brownish-yellow prisms, by adding a soln. of 30 grms. ammonium chromate in 60 c.c. of water to a soln. of 40 grms. crystallized cobalt acetate in 120 c.c. of water and cooled by ice and salt. The salt can be kept for some days at 8°, but it gradually darkens in colour, and loses water; decomposition is rapid at 20°. M. Gröger prepared **ammonium cobaltous diamminoquaterochromate,** $(NH_4)_2CrO_4.3CoCrO_4.2NH_3.3H_2O$, from cobaltous chloride and ammonium chromate. The dark brown product is decomposed by water and by heat. M. Gröger prepared brown **potassium cobaltous chromate,** $K_2CrO_4.CoCrO_4.2H_2O$, from a soln. of one vol. of 3*N*-$CrCl_2$ and 3 vols. of 3*N*-$K_2CrO_4$; and the basic salt **potassium cobaltous oxyquaterochromate,** $K_2CrO_4.CoO.3CoCrO_4.3H_2O$, or $HO.Co.CrO_4.Co.KCrO_4(H_2O)$, by mixing 2 vols. of *N*-$CoCl_2$ and one vol. of *N*-$K_2CrO_4$; or one vol. of the former and 2 vols. of the latter. The dark reddish-brown product consists of microscopic crystals, which are soluble in cold, dil. sulphuric acid, and are decomposed by water forming cobaltous dioxychromate. S. H. C. Briggs prepared **cæsium cobaltous chromate,** $Cs_2CrO_4.CoCrO_4.6H_2O$, as a brown crystalline powder, by mixing 2 grms. of cæsium chromate in 6 c.c. of cold water with a soln. of 1·2 grms. of crystalline cobalt acetate cooled to about −5°.

S. H. C. Briggs prepared a series of **chromatocobaltammines**—*e.g.* **cobaltic chromatopentamminonitrate,** $[Co(NH_3)_5(CrO_4)]NO_3$, by the action of potassium chromate on the aquopentamminonitrate. The salt is moderately soluble in cold water, and the freshly prepared soln. is not precipitated by silver, barium, or lead salts, but precipitation occurs at once in the boiling soln. Similarly, cobalt aquopentamminochloride furnishes brownish-red crystals of **cobaltic chromatopentamminochloride,** $[Co(NH_3)_5(CrO_4)]Cl$. If the mother-liquor is heated to 50° and treated with more potassium chromate, on cooling, it furnishes yellowish-brown prisms of **cobaltic chloropentamminochromate,** $[Co(NH_3)_5Cl)]CrO_4.2\frac{1}{2}H_2O$. If cobaltic chromatopentamminochloride in water at 60° be treated with silver chromate, **cobaltic chromatopentamminochromate,** $[Co(NH_3)_5(CrO_4)]_2CrO_4.3H_2O$, is formed in scaly crystals the colour of silver chromate. P. R. Ray and P. V. Sarkar represented it as a dihydrate, and obtained it by the action of ammonium dichromate and aq. ammonia on freshly precipitated cobalt hydroxide. By treating cobaltic diaquotetramminonitrate with a dil. soln. of potassium chromate, **cobaltic chromatotetramminonitrate,** $[Co(NH_3)_4(CrO_4)_2]NO_3.\frac{1}{2}H_2O$, was formed as a dark reddish-brown crystalline mass, soluble in water; if an excess of potassium chromate is used, **cobaltic chromatotetramminochromate,** $[Co(NH_3)_4(CrO_4)_2]CrO_4.3H_2O$, is formed as a brown crystalline powder. The corresponding dichromate (*q.v.*) was also prepared. By treating cobalt diaquotetramminonitrate with a conc. soln. of potassium chromate, a greenish precipitate of **cobaltic trichromatotetrammine,** $[Co(NH_3)_4(CrO_4)_2]CrO_4.5H_2O$,

$$\left[Co\begin{matrix}(CrO_4)\\(NH_3)_4\end{matrix}-CrO_4-\begin{matrix}(CrO_4)\\(NH_3)_4\end{matrix}Co\right].5H_2O$$

was obtained; and by treating cobalt trinitratotriammine with a soln. of potassium chromate, **cobaltic hydroxychromatotriammine,** $[Co(NH_3)_3(OH)(CrO_4)_2].2H_2O$, was formed—for the dichromate, *vide infra.*

According to R. Tupputi,[33] a soln. of chromic acid dissolves nickel hydroxide or carbonate forming a yellow soln. which deposits a powder soluble in a large excess of the acid. The soln. deposits a non-deliquescent mass of red crystals,

which, according to J. F. John, are resolved at a red-heat into chromic and nickel oxides. If the soln. be treated with nickel carbonate, or with alkali-lye, R. Tupputi observed that a reddish-yellow insoluble powder of a **nickel oxychromate** is deposited; and H. Stokes, and F. J. Malaguti and M. Sarzeau observed that a basic salt is deposited when a soln. of nickel sulphate is mixed with potassium chromate. C. Freese added that the yellowish-brown product is scarcely attacked by cold potash-lye, but all the chromium is extracted by boiling lye. F. J. Malaguti and M. Sarzeau represented its composition by $4NiO.CrO_3.6H_2O$; C. Freese, by $3NiO.CrO_3.3H_2O$; and E. A. Schmidt obtained precipitates ranging from $3NiO.CrO_3.6H_2O$ to $2NiO.CrO_3.6H_2O$ by varying the conc. of the soln. employed. S. H. C. Briggs said that while nickel chromate is insoluble in water, it is not precipitated from nickel salt soln., and it must therefore be polymerized. It is formed by heating nickel carbonate and a soln. of chromic acid in a sealed tube at 260°. The black crystals of **nickel chromate,** $NiCrO_4$, are washed with water, alcohol, and ether. They are insoluble in hot dil. nitric acid, and are slowly attacked by conc. nitric acid or aqua regia. G. L. Clark found that **nickel hexamminochromate,** $Ni(NH_3)_6CrO_4$, has a vap. press. of 760 mm. at 408°.

S. H. C. Briggs obtained **ammonium nickel chromate,** $(NH_4)_2CrO_4.NiCrO_4.6H_2O$, by adding a soln. of ammonium chromate to a soln. of a nickel salt; and M. Gröger obtained it by adding $3N$-$(NH_4)_2CrO_4$ to half its vol. of $N$-$NiCl_2$, and allowing the mixture to stand for some time. The green crystals can be recrystallized from water at 40° without change. G. L. Clark studied the relations between the at. vol. and the stability. S. H. C. Briggs showed that when treated with ammonia, **ammonium nickel diamminochromate,** $(NH_4)_2CrO_4.NiCrO_4.2NH_3$, is formed. The product loses water and ammonia when it is heated, and it decomposes suddenly between 200° and 300°. M. Gröger obtained the basic salt, **ammonium nickel dihydroxyquaterchromate,** $3(NH_4)_2CrO_4.Ni(OH)_2.NiCrO_4$, from a mixture of a cold, sat. soln. of ammonium chromate with a fifth of its vol. of $3N$-$NiCl_2$. The yellowish-brown crystals are stable in air; they are decomposed by water with the separation of a basic nickel chromate; and form with water a yellowish-green soln. which when evaporated at a low temp. yield ammonium chromate, and ammonium nickel chromate. M. Gröger mixed $3N$-$Na_2CrO_4$ with half its vol. of $N$-$NiCrO_4$ and obtained a brown, amorphous precipitate, probably a basic sodium nickel chromate; and by mixing $3N$-$K_2CrO_4$ with half its vol. of $N$-$NiCrO_4$, a reddish-brown precipitate is formed which, when allowed to stand under its mother-liquor, becomes crystalline **potassium nickel chromate,** $K_2CrO_4.NiCrO_4.2H_2O$. This *dihydrate* is stable in air, and loses no water on the water-bath. It is decomposed by water with the separation of a basic salt. S. H. C. Briggs obtained the *hexahydrate* by adding 8 grms. of potassium chromate in 14 c.c. of water to 8 grms. of nickel acetate in 27 c.c. of water at −6°. The yellowish-green crystals dissolve in water with decomposition. The hexahydrate forms isomorphous mixtures with the corresponding sulphate. S. H. C. Briggs also prepared **rubidium nickel chromate,** $Rb_2CrO_4.NiCrO_4.6H_2O$; and **cæsium nickel chromate,** $Cs_2CrO_4.NiCrO_4.6H_2O$, in an analogous way. Both salts are decomposed by water.

The normal chromates of the platinum metals have not been prepared. According to T. Thomson,[34] a soln. of hydrochloroplatinic acid, when treated with potassium chromate furnishes a dark red precipitate containing potassium chloroplatinate. P. T. Cleve, and G. B. Buckton found that an ammoniacal soln. of platinous tetramminodichromate furnishes a yellow powder consisting of microscopic tablets of **platinous tetramminochromate,** $[Pt(NH_3)_4]CrO_4$. The same salt is formed by precipitation from a soln. of platinous chloride by potassium chromate. P. T. Cleve prepared **platinic dinitratotetramminochromate,** $[Pt(NH_3)_4(NO_3)_2]CrO_4$, by treating the corresponding chloride with potassium chromate and drying the product at 100°. The lemon-yellow product detonates sharply when heated; it is insoluble in water. He also prepared **platinic dichlorotetramminochromate,** $[Pt(NH_3)_4Cl_2]CrO_4$, in an analogous manner from the correspond-

ing nitrate. So also with **platinic hydroxysulphatotetramminochromate,** $[Pt(NH_3)_4(OH)(SO_4)]CrO_4.2H_2O$; and with **platinic hydroxychlorotetramminochromate,** $[Pt(NH_3)_4(OH)Cl]CrO_4$. S. G. Hedin prepared **platinic sulphatotetrapyridinochromate,** $[Pt(C_5H_5N)_4(SO_4)]CrO_4.6H_2O$; and C. Enebuske, **platinic chromatobisethylsulphide,** $Pt\{(C_2H_5)_2S\}_2CrO_4$.

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## § 16. The Dichromates

H. Moser,[1] Y. T. Gerassimoff, and others obtained **ammonium dichromate**, $(NH_4)_2Cr_2O_7$, by evaporating a soln. of chromic acid half sat. with ammonia. Y. T. Gerassimoff said that double decomposition with ammonium chloride and

sodium dichromate gives an impure product. S. Darby, J. S. Abel, and J. S. Abel and H. Richmond showed that if the chromic acid is contaminated with sulphuric acid, that salt is easily freed from that contamination by recrystallization. R. Segalle obtained ammonium dichromate by heating an ammoniacal soln. of a mol of potassium dichromate until the liquid has a garnet-red colour; and then evaporating for crystallization. F. A. H. Schreinemakers' observations on the equilibrium conditions are summarized in Fig. 29. Analyses were reported by S. Darby, M. Gröger, M. Siewert, J. Schabus, and J. S. Abel and H. Richmond.

The yellowish-red crystals were found by C. F. Rammelsberg to be monoclinic prisms with the axial ratios $a:b:c=1{\cdot}0271:1:1{\cdot}7665$, and $\beta=93°\,42'$. The (101)-cleavage is clear, and the (010)-cleavage incomplete. Observations on the crystals were also made by H. J. Brooke, J. Schabus, and A. J. Weiss. G. N. Wyrouboff noted some resemblances between the crystals and those of triclinic potassium dichromate; but the two salts are not isomorphous. B. Gossner and F. Mussgnug found that the X-radiograms showed that the monoclinic crystals have a cell with $a=7{\cdot}78$ A., $b=7{\cdot}54$ A., and $c=13{\cdot}27$ A., with $\beta=93°\,42'$. Unit cell contains 4 mols. A. Duffour said that the crystals are isomorphous with the monoclinic form of potassium dichromate. H. Schiff gave 2·367 for the sp. gr.; F. W. Clarke, and G. N. Wyrouboff, 2·150; and E. Moles and F. Gonzalez, 2·16 at 25°. K. F. Slotte found the sp. gr. of soln. of ammonium dichromate with 6·85, 13·0, and 19·93 per cent. of the dichromate to be respectively 1·0393, at 12°, 1·0782 at 10·5° and 1·1258 at 12°; and the viscosities (water 100) to be respectively 98·9, 99·1, and 100·6 at 10°; 76·8, 78, 80·2, at 20°; 62·5, 63·9 and 66·4 at 30°; and 51·9, 53·3, and 55·7 at 40°. H. Moser, and E. Jäger and G. Krüss said that the salt is stable in air; and J. S. Abel and H. Richmond, that it is stable at 100°. A. Maus, R. Böttger, E. Moles and F. Gonzalez, and A. A. Hayes found that the salt decomposes at a temp. below redness leaving a residue of chromic oxide. The reaction is attended by the emission of light, and may be by a feeble detonation, especially, as shown by M. Siewert, if it be quickly heated in a test-tube. The gaseous products of the reaction were found by J. S. Abel and H. Richmond, and A. Levy to be nitrogen and water, but S. Darby observed that some ammonia gas may be produced; and M. Siewert, and W. M. Hooton, some nitric oxide and oxygen. C. N. Hinshelwood and E. J. Bowen studied the rate of decomposition at 219°. W. C. Ball said that at 185°–205° the salt darkens in colour, and decomposes slowly with the evolution of water, nitrogen, and ammonia; and after six days' heating, there remains a black residue approximating $3CrO_2.H_2O$; and if the heating be interrupted when the salt is half decomposed, an insoluble black product, approximating $Cr_2O_3.2CrO_3.2NH_3.H_2O$, is obtained. W. M. Hooton found that if ammonium dichromate be heated in air, below the inflammation temp. 190°, the end-product has the composition $2CrO_2.H_2O$; and if heated in the absence of oxygen, $H_2Cr_2O_4$—*vide supra* for E. Maumené's observations on ammonium chromate. E. Moles and F. Gonzalez observed that tranquil decomposition occurs at about 225°, and that the oxidation of the "ammonium" to nitrogen is most complete where the reaction occurs most rapidly. The black residue thereby obtained is chromium peroxide. Y. T. Gerassimoff found that the aq. soln. is slightly decomposed when it is boiled.

R. Böttger said that if an intimate mixture of the dichromate with half its weight of picric acid be brought in contact with a glowing splint, it decomposes with sparking forming pale green, flocculent chromic oxide. C. N. Hinshelwood and E. J. Bowen studied the rate of the thermal decomposition of ammonium dichromate. With the explosive decomposition of the salt, M. Berthelot found that 7·8 Cals. are developed; and he gave for the heat of formation: $2H_2CrO_4(800_{aq.})+2NH_4OH(1600_{aq.})=(NH_4)_2Cr_2O_{7aq.}+24$ Cals at 12°; E. Moles and F. Gonzalez, 23·275 Cals., and F. Morges, 26·988 Cals. at 19·5°. M. Berthelot gave for the reaction $(NH_4)_2Cr_2O_{7aq.}+2NH_4OH_{aq.}=2(NH_4)_2CrO_{4aq.}+20{\cdot}4$ Cals.; for precipitated chromic oxide, $2Cr(OH)_3+2NH_4OH_{aq.}+3O=(NH_4)_2Cr_2O_{4aq.}+34{\cdot}6$ Cals. at 12°; and 47

Cals. with the solid dichromate; $(NH_4)_2CrO_{4solid}+CrO_{3solid}=(NH_4)_2Cr_2O_{7solid}$ +11·300 Cals. For the heat of decomposition, $(NH_4)_2Cr_2O_7=Cr_2O_3+N_2+4H_2O$ $+(78·000+Q)$ cals., where $Q$ denotes the heat of transformation of chromic oxide. For the reducing action of ammonia on chromium trioxide: $2CrO_3+2NH_3=Cr_2O_3$ $+3H_2O_{gas}+N_2+146·6$ Cals.; the heat of soln. of a mol of the salt in 560 mols of water at 13° is −12·44 Cals.; E. Moles and F. Gonzalez gave −12·904 Cals.; P. Sabatier gave −5·8 Cals. for the heat of soln. of a mol of the salt in 200 mols of water. P. Sabatier measured the absorption spectrum. S. Schlivitch observed a photovoltaic effect with soln. of ammonium dichromate and platinum electrodes. H. Moser said that the aq. soln. has a saline taste, and reddens litmus. The salt is less soluble than ammonium chromate. E. Moles and F. Gonzalez gave for the solubility 23·88 per cent. at 16°, and 28·63 per cent. at 25°. F. A. H. Schreinemakers found that 100 grms. of water at 30° dissolve 47·17 grms. of ammonium dichromate. The salt in aq. soln. is less hydrolyzed than the monochromate, and Y. T. Gerassimoff found that the solubilities of ammonium dichromate, $S$ grms. of salt per 100 grms. of water, working on cooling and heating systems, are:

| | | 0° | 20° | 40° | 60° | 80° | 100° |
|---|---|---|---|---|---|---|---|
| $S$ | Cooling | 18·40 | 36·0 | 58·7 | 86·0 | — | — |
| | Heating | 18·13 | 35·3 | 58·4 | 86·0 | 115·0 | 155·6 |

and the disturbance is probably due to undercooling. The solubility curves for the system $(NH_4)_2Cr_2O_7$–$(NH_4Cl)_2$–$H_2O$ at different temp., are summarized in Fig. 65—mols of salt per 1000 mols of water; *confer* Fig. 1, **1**. 11, 1. A. Naumann and A. Rücker calculated that in a $N$-soln. at the b.p., 0·0108 per cent. is hydrolyzed. B. Reinitzer said that the salt is soluble in absolute alcohol. W. P. Jorissen discussed the limits of the reaction of ammonium dichromate with potassium chloride and sulphate.

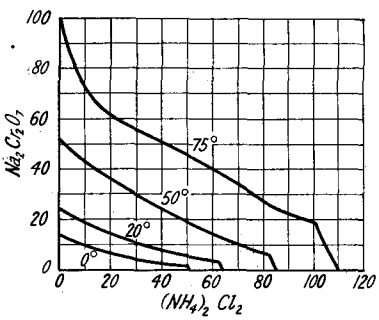


FIG. 65.—The Effect of Ammonium Chloride on the Solubility of Ammonium Dichromate.

According to C. F. Rammelsberg,[2] if chromic acid or nitric acid be added to a soln. of lithium chromate, the liquid furnishes deliquescent crystals of **lithium dichromate,** $Li_2Cr_2O_7.2H_2O$. The conditions of equilibrium are illustrated by Fig. 31. The black plates have curved surfaces. L. Schulerud found that the water of crystallization is completely lost at 130°, and the salt melts at a higher temp. with the evolution of oxygen. The salt can be recrystallized from water without decomposition; and F. A. H. Schreinemakers observed that 100 grms. of water at 30° dissolve 130·4 grms. of $Li_2Cr_2O_7$. A. Heydweiller found the sp. gr., and eq. conductivity, at 18°, to be:

| | 0·2$N$- | 0·5$N$- | $N$- | 2$N$- |
|---|---|---|---|---|
| Sp. gr. | 1·01581 | 1·03928 | 1·0780 | 1·1540 |
| $\lambda$ | 73 | 66·1 | 58·7 | 47·7 |

The preparation of **sodium dichromate,** $Na_2Cr_2O_7.2H_2O$, is effected by methods similar to those employed for the potassium salt. J. d'Ans and J. Löffler [3] observed it amongst the products of the action of sodium hydroxide on chromic oxide. M. Siewert said that it is not produced by partially saturating sodium chromate with nitric acid, but it is produced by dissolving sodium chromate in a slight excess of chromic acid, and evaporating the liquid over sulphuric acid in vacuo. G. Bessa discussed the manufacture of sodium dichromate. R. Kissling found that commercial samples contained 83·79 to 92·84 per cent. $Na_2Cr_2O_2$; and with seven different samples, 23 days' exposure resulted in the absorption of 60 per cent. of

water in each case. B. Neumann and C. Exssner discussed the conversion of sodium chromate to dichromate in aq. soln. by carbon dioxide under press.

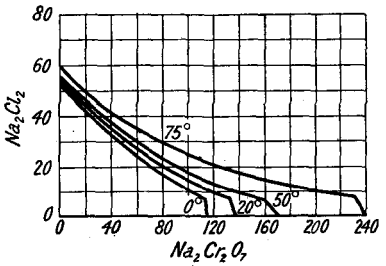


FIG. 66.—The Effect of Sodium Chloride on the Solubility of Sodium Dichromate.

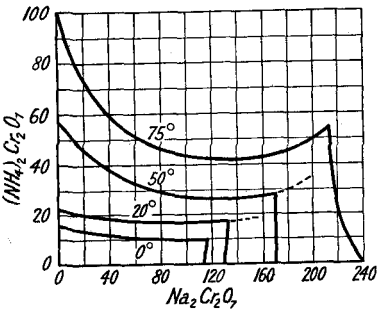


FIG. 67.—The Effect of Ammonium Dichromate on the Solubility of Sodium Dichromate.

E. Müller and E. Sauer found that in the conversion of soln. of sodium chromate to dichromate and hydroxide by electrolysis, if the anolyte is a soln. of sodium chromate and the catholyte one of sodium hydroxide the yield is less than if sodium chromate is used in both compartments. A. Lottermoser and K. Falk found that better yields are obtained with three compartment cells with sodium chromate in all three compartments rather than with sodium hydroxide as catholyte and sodium chromate in the other two compartments. This is because in the former case circumstances are least favourable for the migration of HO-ions into the anode compartment. I. Stsherbakoff studied the electrolysis of soln. of sodium chromate using a mercury cathode. T. W. Richards and G. L. Kelley found that sodium dichromate can be readily purified from potassium salts and sulphates by recrystallization from water a number of times. The conditions of equilibrium, worked out by F. A. H. Schreinemakers, are illustrated by Fig. 34. F. Mylius and R. Funk gave 83° for the transition temp. from the *dihydrate* to the anhydrous salt. The solubility, *S* per cent., of sodium dichromate in water is:

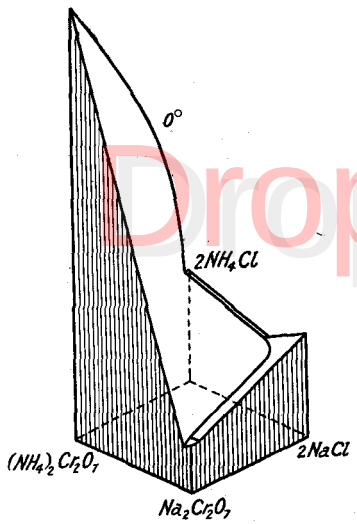


FIG. 68.—The Quaternary System: $(NH_4)_2Cr_2O_7$–$Na_2Cr_2O_7$–$Na_2Cl_2$–$(NH_4Cl)_2$ at 0°.

| | 0° | 10° | 20° | 40° | 60° | 80° | 83° | 93° | 98° |
|---|---|---|---|---|---|---|---|---|---|
| *S* . | 62·0 | 63·0 | 64·3 | 68·8 | 73·9 | 79·4 | 80·7 | 81·20 | 81·24 |
| Solid phase | $Na_2Cr_2O_7.2H_2O$ | | | | | | $Na_2Cr_2O_7$ | | |

A. Stanley found that 100 parts of water dissolve 107·2 parts of $Na_2Cr_2O_7$ at 0°; 109·2 parts at 15°; 116·6 parts at 30°; 142·8 parts at 80°; 162·8 parts at 100°; and 209·7 parts at 139°. F. A. H. Schreinemakers found that at 30° water dissolves 66·4 per cent. of $Na_2Cr_2O_7$. Y. I. Gerassimoff found that the solubility curves for the system $Na_2Cr_2O_7$–NaCl–$H_2O$, at different temp., are summarized in Fig. 66—mols of salt per 100 mols of water—*confer* Fig. 1, **1**. 11, 1. The solubility curves for the system $(NH_4)_2Cr_2O_7$–$Na_2Cr_2O_7$–$H_2O$, at different temp., are

summarized in Fig. 67—mols of salt per 1000 mols of water—*confer* Fig. 1, 1. 11, 1. The equilibrium diagrams for the quaternary systems $(NH_4)_2Cr_2O_7$–$Na_2Cr_2O_7$–$Na_2Cl_2$–$(NH_4Cl)_2$, at 0° and 75° are indicated in Figs. 68 and 69.

The dihydrate furnishes hyacinth-red, thin, six-sided prisms which, according to M. Siewert, are triclinic, but, according to L. Münzing, are monoclinic. G. N. Wyrouboff gave for the axial ratios of the monoclinic crystals $a:b:c=0{\cdot}5698:1:1{\cdot}824$, and $\beta=94°\,55'$; while L. Münzing gave $0{\cdot}5912:1:0{\cdot}5698$, and $\beta=85°\,5'$. The optic axial angle $2V=83°\,54'$; and the optical character is positive. The deliquescent crystals were found by A. Stanley to have a sp. gr. 2·5246 at 13°. According to A. Stanley, the sp. gr. of the aq. soln. is:

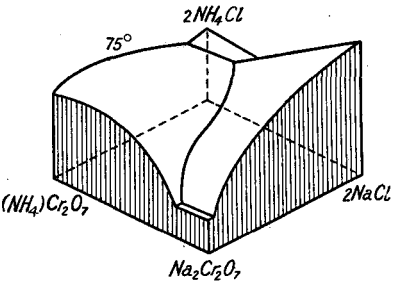


FIG. 69.—The Quaternary System: $(NH_4)_2Cr_2O_7$–$Na_2Cr_2O_7$–$Na_2Cl_2$–$(NH_4Cl)_2$ at 75°.

| $Na_2Cr_2O_7$ . | 1 | 5 | 10 | 20 | 30 | 40 | 50 per cent. |
|---|---|---|---|---|---|---|---|
| Sp. gr. . | 1·007 | 1·035 | 1·071 | 1·141 | 1·208 | 1·280 | 1·343 |

while H. C. Jones and H. P. Basset gave at 18°,

| $Na_2Cr_2O_7$ . | 1·31 | 2·59 | 5·09 | 7·50 | 9·83 | 18·40 | 26·90 per cent. |
|---|---|---|---|---|---|---|---|
| Sp. gr. . | 1·0096 | 1·0190 | 1·0377 | 1·0568 | 1·0756 | 1·1491 | 1·2285 |

L. J. Simon measured the viscosities of soln. of sodium dichromate—*vide supra*, potassium chromate. F. Mylius and R. Funk observed that a soln. sat. at 18° contains 63·92 per cent. of $Na_2Cr_2O_7$, and has a sp. gr. 1·745; F. Rüdorff found that the salt does not decompose when in aq. soln. I. Traube found the drop-weight of the molten anhydrous salt to be 262·0 mgrms. A. Stanley found that the dihydrate becomes anhydrous above 303°; it melts at 320°, and decomposes at 400° with the evolution of oxygen. P. L. Robinson and co-workers observed no transition phenomenon when the salt is cooled between 300° and 70°. H. C. Jones and H. P. Bassett found that soln. with 0·1, 0·2, and 0·4 mols per litre lower the f.p. of water respectively 0·490°, 0·946°, and 1·872°. A. Stanley said that the sat. aq. soln. boils at 139°. J. Thomsen gave for the heat of formation: $2H_2CrO_4(800_{aq.})+2NaOH(400_{aq.})=Na_2Cr_2O_{7aq.}+26{\cdot}268$ Cals. at 18°; and F. Morges, $2H_2CrO_{4aq.}+2NaOH_{aq.}=Na_2Cr_2O_7+26{\cdot}076$ Cals. at 19·5°.

H. Dufet found the indices of refraction of the crystals of the dihydrate to be $\alpha=1{\cdot}7510$, $\beta=1{\cdot}6994$, and $\gamma=1{\cdot}6610$ for the *D*-line. P. Walden measured the electrical conductivity of aq. soln. at 25°; while H. C. Jones and co-workers found for the molar conductivity, $\mu$ mho, and for the percentage ionization, $\alpha$, calculated from $\mu/\mu_\infty$, with a mol of the salt in $v$ litres of water:

| $v$ . . . | 8 | 16 | 32 | 128 | 512 |
|---|---|---|---|---|---|
| $\mu$ 0° . . | 92·18 | 96·57 | 101·25 | 106·8 | 106·1 |
| $\mu$ 15° . . | 136·5 | 143·5 | 148·4 | 158·3 | 158·3 |
| $\mu$ 25° . . | — | 176·3 | 182·7 | 194·7 | 194·4 |
| $\mu$ 35° . . | — | 211·4 | 219·5 | 233·5 | 234·6 |
| $\alpha$ 0° . . | 87·5 | 91·3 | 95·7 | 100·0 | 100·0 |
| $\alpha$ 35° . . | — | 89·9 | 93·3 | 100·0 | 100·0 |

H. C. Jones calculated from the sp. gr., f.p., and conductivity data that soln. with $M$ mols per litre have $H$ mols of water in combination with a mol of the salt, when $M$ is 0·1, 0·2, 0·3, and 0·4, $H$ is respectively 20·5, 9·7, 6·5, and 7·9. A. Poirot found that the emission of anodic rays with purified sodium dichromate is regular and stable. The emission starts suddenly below the m.p. of the salt. The anode is surrounded by a yellowish glimmer. There is an intense yellow spot on the cathode where it is hit by the anodic rays. The spectra of the anodic and cathodic lights

were examined. H. Ollivier studied Verdet's constant, and the paramagnetism of the salt. E. C. Franklin and C. A. Kraus said that the salt is insoluble in liquid ammonia; A. Naumann, that it is insoluble in acetone; and B. Reinitzer that 100 c.c. of a soln. in alcohol contain 5·13 grms. of $Na_2Cr_2O_7.2H_2O$. The alcoholic soln. decomposes rapidly. V. K. la Mer and C. L. Read found that the reaction between sodium hydroxide and dichromate is unimolecular with respect to the dichromate and the velocity constant is $k=529$ per min., and the heat of reaction 15,320 cals. per mol of dichromate. The results are best interpreted as involving the reactions: $Cr_2O_7'' + H_2O \rightleftharpoons 2HCrO_4'$ (slow), with $Q=-13{,}640$ cals. per mol $Cr_2O_7''$; $HCrO_4' \rightleftharpoons H' + CrO_4''$ (rapid), with $Q=780$ cals. per mol $HCrO_4'$; and $H' + OH' = H_2O$ (rapid).

The manufacture of **potassium dichromate,** $K_2Cr_2O_7$, has been discussed in connection with the extraction of chromium from chromite, etc. F. Tassaert[4] obtained it by mixing soln. of chromic acid and potassium hydroxide in such proportions that the soln. reacts neither acidic nor alkaline, and evaporating the liquid. The dichromate first separates out, and the mother-liquid, then reacting alkaline, furnishes the monochromate. It is also obtained from acidified soln. of potassium chromate. E. Gray, and V. S. Yatloff also described its preparation. The conditions of equilibrium have been studied by F. A. H. Schreinemakers, F. Flöttmann, and I. Koppel and E. Blumenthal, and the results are summarized in Figs. 36 to 41. Y. R. Goldstein, and H. Pincass discussed the transformation from chromate to dichromate by carbon dioxide; and I. Obreimoff and W. J. de Haas, the colour changes at low temp. The bright-red, rectangular, four-sided tabular or prismatic crystals are triclinic pinacoids which, according to J. Schabus, have the axial ratios $a:b:c=0{\cdot}5575:1:0{\cdot}5511$, and $\alpha=82°\ 0'$, $\beta=90°\ 51'$, and $\gamma=83°\ 47'$. The (010)-cleavage is perfect; and the (100)- and the (001)-cleavages are distinct. G. N. Wyrouboff also made some crystallographic observations. B. Gossner and F. Mussgnug showed that the X-radiograms of the triclinic salt correspond with a unit cell having 4 mols., and $a=7{\cdot}50$ A., $b=7{\cdot}38$ A., and $c=13{\cdot}40$ A., whilst $\alpha=82°\ 0'$, $\beta=96°\ 13'$, and $\gamma=90°\ 51'$. H. Dufet observed that the optical character is positive; and that the optic axial angles $2E=98°\ 58'$ and $2V=51°\ 53'$ for the *D*-line; and $2V=52°\ 24'$ for the Li-line. A. Beer observed that the crystals are pleochroic. H. Baumhauer studied the corrosion figures. A. Schubnikoff showed that a crystal, suspended in a slighly supersaturated soln. rotating on a horizontal axis, grows so that the (001)-face is bright and smooth, while the $(00\bar{1})$-face is dull and rough, while the other parallel faces are not the same size or are absent. This is taken to show that the crystals of the dichromate belong to the asymmetric class of the triclinic system. A. Hettich and A. Schleede made observations on the crystals. E. Pietsch and co-workers found that the attack on the crystals by sulphuric acid begins at the corners and edges. D. N. Arteméeff, R. Marc, M. le Blanc and W. Schmandt, H. Jeannel, M. Kimura, and C. Tomlinson studied the growth of crystals in supersaturated soln. The rate of growth of the crystals is not solely a diffusion phenomenon as is the case with the speed of dissolution—*vide infra*. H. A. Miers said:

> If a drop of strong soln. of potassium dichromate, placed upon a microscope-slide, be observed under the microscope as it crystallizes, and if the drop be sufficiently thin, it will generally be found that the following events take place: The first crystals make their appearance at the edges of the drop and after growing rapidly for a short period as branching fibres, they begin to grow quietly in the form of plates or flattened rods presenting the characteristic form of the crystals of this substance. These crystals continue to grow uniformly, but after a short period, at a distance from the growing crystals, and at some spot where the drop is thin, a fresh crystalline growth starts suddenly from a point, and extends with great rapidity in all directions in the form again of branching needles and fibres. After a short period this rapid growth ceases and each of the fibres swells out at the end into a well-defined crystal and continues to grow slowly and uniformly as a single, regular plate. The process may be repeated by the sudden development of a new spontaneous growth in another portion of the drop, and the same succession of events may be repeated again and again. Sometimes these successive growths constitute a series of

rings approximately parallel to the edges of the drop which follow one another till the centre of the drop is reached.

An illustration of a drop of the dichromate in the act of crystallization is shown **1**. 11, 3, Fig. 11. The phenomenon connected with crystallizations in labile and metastable soln.—**1**. 9, 6, Fig. 14—gave a possible explanation for the periodic crystallization of soln. of potassium dichromate. E. Pietsch and co-workers studied the attack at the corners and edges of the crystals by conc. sulphuric acid, and by an ethereal soln. of hydrogen dioxide. W. von Behren and J. Traube studied the phenomenon attending the dissolution and crystallization of the salt. E. S. Hedges obtained spiral forms of rhythmic crystallization; and E. N. Gapon studied the rate of crystallization.

Crystals appear at the edge of the drop where, owing to evaporation or cooling, the soln. is sufficiently strong to be in the labile condition, and proceed as rapidly growing fibres; but so soon as these have by their growth reduced the strength of the soln. in their neighbourhood to the metastable state they continue to grow quietly and uniformly; presently, however, at some point sufficiently distant from the growing crystals to be also in the labile state, crystallization starts afresh, either spontaneously or perhaps through inoculation by a crystalline speck falling into the drop from the air. This again proceeds as the rapid, fibrous growth, characteristic of the labile condition, until again the liquid passes into the metastable state and the growth is slow.

Soln. with 17·266 (28·5°), 20·00 (32·2°) and 29·09 (43·5°) grms. of salt in 100 parts of water, and sat. at the temp. named, were labile respectively at 18·5°, 22°, and 34°. M. Volmer and A. Weber discussed the formation of nuclei in undercooled soln. C. Decharne observed the crystallization of the dichromate from a soln. mixed with gum, when under the influence of a strong magnetic field. G. Brügelmann said that potassium dichromate forms isomorphous mixtures with pentahydrated cupric sulphate, but J. C. G. de Marignac did not agree. S. F. Schemtschuschny studied the formation of isomorphous mixtures with potassium chloride; and C. F. Rammelsberg, P. Groth, L. Stibing, A. Sella, A. Fock, H. le Chatelier, and C. von Hauer, solid soln. with potassium pyrosulphate. C. von Hauer observed that the crystals of the dichromate take up potassium sulphate when that salt is present in the liquid during the crystallization.

Triclinic potassium dichromate may be called the $\alpha$-form; there is also a monoclinic $\beta$-form. E. Mitscherlich observed that when the molten dichromate is slowly cooled, crystals are formed which afterwards decrepitate; O. Lehmann showed that the change is reversible; G. Tammann found that there is a large change in vol. at 240°, accompanied by an imperceptible thermal change; G. Tammann and Q. A. Mansuri measured the rate of crystallization of the powdered salt and found that it commences at 160° with particles over 1 mm. diam., at 166° with particles between 1·0 and 0·3 mm., and at 158·5°–163° with particles smaller than 0·3 mm., and G. N. Wyrouboff concluded that potassium dichromate exists in three forms: (i) a monoclinic form stable near the m.p.; (ii) a triclinic form stable at the ordinary temp.; and (iii) a second triclinic form stable in a narrow range of temp. between the other two forms. S. F. Schemtschuschny added that the transition temp., $\alpha$-$K_2Cr_2O_7$=$\beta$-$K_2Cr_2O_7$, is 236°; and P. L. Robinson and co-workers gave 236·8°. P. L. Robinson and co-workers added that the salt separates from the fused state in a compact mass of dark brownish-red, tabular crystals with marked reduction in volume. On further cooling, the crystals change to a loose, orange-red powder. The existence of G. N. Wyrouboff's second triclinic form has not been confirmed, so that the crystals which first separate from the cooling liquid are doubly refracting—probably monoclinic, and at about 236° these crystals pass into the ordinary triclinic form. O. Hauser and H. Herzfeld observed that when hot, conc. soln. of potassium dichromate and hot potassium thiocyanate are mixed, the dichromate crystallizes on cooling in yellowish-brown, doubly-refracting, monoclinic plates. The sp. gr. of this form is 2·10, whereas that of the ordinary triclinic variety is 2·67. The monoclinic dichromate is unstable, and is transformed into

the triclinic salt when kept in contact with its sat. soln., or in moist air. It seems probable that this form of the potassium salt is isomorphous with monoclinic ammonium dichromate. A. Duffour also observed that if a considerable excess of aluminium sulphate is added to a soln. of potassium monochromate, some aluminium hydroxide is precipitated, and when the soln. is concentrated by heat, potassium dichromate separates out in monoclinic and triclinic crystals. The monoclinic crystals are isomorphous with those of rubidium and ammonium dichromates. P. L. Stedehouder and P. Terpstra found for the monoclinic form $a:b:c$ $=1{\cdot}0123:1:1{\cdot}7675$, and $\beta=88°\ 4{\cdot}5'$; and the optic axial angle of the pleochroic crystals $2V=66°\ 14'$. The X-radiograms gave $a=7{\cdot}42$ A., $b=7{\cdot}35$ A., $c=12{\cdot}97$ A., and $\beta=91°\ 55°$, with 4 mols. per unit cell which is face-centred on the (100)-side. According to A. Duffour, the axial ratios for the three forms are $a:b:c$ $=1{\cdot}0167:1:1{\cdot}7716$, and $\beta=91°\ 55'$ for $K_2Cr_2O_7$; $1{\cdot}0202:1:1{\cdot}8081$, and $\beta=98°\ 28{\cdot}5'$ for $Rb_2Cr_2O_7$; and $1{\cdot}0271:1:1{\cdot}7663$, and $\beta=93°\ 42'$ for $(NH_4)_2Cr_2O_7$. Although the monoclinic crystals of the dichromate are the unstable form, they exhibit false equilibrium, and can be kept in contact with triclinic crystals in the cold without any appreciable change. They dissolve in a soln. saturated with respect to triclinic crystals at 12·5°, whereas triclinic crystals are unaffected under the same conditions. On heating, the monoclinic crystals decrepitate, and then behave like the triclinic crystals. The following description of potassium dichromate refers to the stable, triclinic forms unless stated otherwise. A. Duffour, and A. F. Hallimond discussed the isodimorphism of potassium and ammonium dichromates; H. E. Buckley, the effect of dichromates on the crystallization of sodium chlorate.

C. J. B. Karsten gave 2·603 for the sp. gr. of potassium dichromate; J. Schabus, 2·689; L. Playfair and J. P. Joule, 2·692 at 3·9°; and H. Schiff, 2·721. H. G. F. Schröder gave 2·702 for that which had been melted, 2·751 for that which had been melted and disintegrated, and 2·702 for the powdered salt. P. Kremers, and G. T. Gerlach gave for the sp. gr. of soln. at 19·5°/19·5°:

| $K_2Cr_2O_7$ . | 1 | 3 | 5 | 7 | 9 | 11 | 13 | 15 per cent. |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. . | 1·867 | 1·022 | 1·037 | 1·050 | 1·065 | 1·080 | 1·097 | 1·110 |

F. Flöttmann gave for the sp. gr. at 15°, 20°, and 25°, respectively, 1·0635, 1·0768, and 1·0916. For A. Heydweiller's observations, *vide infra*. J. A. Ewing and J. G. MacGregor gave for soln. with 0·99, 2·44, 4·76, and 7·69 per cent. $K_2Cr_2O_7$ the respective values 1·0069, 1·0172, 1·0345, and 1·0561 at 10°/4°; and F. Fouqué gave for soln. with 5·9 grms. of $K_2Cr_2O_7$ per 1000 grms. of water 1·0045 at 0°/4°; 1·0037 at 16·4°/4°; 1·9812 at 75·5°/4°; and 1·9651 at 99°/4°; for soln. with 37·3 grms. of salt per 1000 grms. of water, 1·0257 at 0°; 1·0234 at 19·6°; 1·0030 at 69·6°; and 0·9843 at 99°; and for soln. with 89·2 grms. of salt per 1000 grms. of water, 1·0635 at 16°; 1·0349 at 79°; and 1·0221 at 99·5°. Observations on the sp. gr. were also made by E. F. Anthon, R. L. Datta and N. R. Dhar. R. Lorenz and W. Herz studied the critical density of this and related salts. J. N. Rakshit studied the contraction which occurs when potassium dichromate is dissolved in water, and in ethyl alcohol. K. F. Slotte found the sp. gr. of soln. of potassium dichromate with 4·71 and 6·97 per cent. $K_2Cr_2O_7$ to be respectively 1·0325 at 11°, and 1·0493 at 10·6°; and the viscosities (water 100) respectively 98·9, and 98·6 at 10°; 76·2 and 76·9 at 20°; 61·7 and 62 at 30°; and 51·1 and 51·4 at 40°. A. Kanitz gave for $2N$-, $4N$-, and $8N$-soln. the respective viscosities 1·0061, 1·0034, and 0·9999 (water unity) at 25°. L. J. Simon measured the viscosity of soln. of the salt—*vide supra*, potassium chromate. I. Traube gave 235·9 mgrms. for the drop-weight of the molten salt. R. Lorenz and W. Herz gave 123·6 for the surface tension at the b.p., and 140·6 at the m.p. R. Lorenz and H. T. Kalmus gave for the viscosity $\eta$ in C.G.S. units:

| | 397° | 417° | 437° | 457° | 477° | 497° | 507° |
|---|---|---|---|---|---|---|---|
| $\eta$ . | 0·1339 | 0·1187 | 0·1059 | 0·0938 | 0·0823 | 0·0715 | 0·0664 |

F. Rüdorff found that the salt in aq. soln. diffuses through a membrane without dissociation. According to T. Sabalitschka and G. Kubisch, when soln. of potassium dichromate are dialyzed, the ratio K : Cr outside the dialyzer is not constant but is greater than 1. Chromic acid dialyzed more quickly than potassium chromate. Hence, it was inferred that potassium dichromate is partly decomposed into normal chromate and trichromate in dil. aq. soln.: $2K_2Cr_2O_7 \rightleftharpoons K_2CrO_4 + K_2Cr_3O_{10}$. L. Playfair and J. P. Joule found the coeff. of thermal expansion—cubical—of the salt to be 0·0122 between 0° and 100°. F. E. Neumann gave 0·1857 for the sp. ht.; while H. Kopp gave 0·186 between 21° and 52°; H. V. Regnault, 0·186 between 16° and 98°; and P. Nordmeyer and A. L. Bernoulli, 0·1386 between −186° and 20°. T. Thomson observed that the dichromate decrepitates when heated, and melts at a temp. much below redness, forming a transparent, red liquid, which on cooling solidifies to a red fibrous mass, which falls to pieces spontaneously—*vide supra*. C. Schubert, and W. Hempel and C. Schubert, observed that the evolution of gas sets in at 500°, and has not ceased as the temp. is raised to 1500°; the reaction is represented $4K_2Cr_2O_7 = 3O_2 + 2(Cr_2O_3.2K_2CrO_4)$. A. Eucken and G. Kuhn gave 0·00395 to 0·00417 for the sp. ht. of large crystals at −190°; and at 0°, 0·00428 to 0·00429. S. F. Schemtschuschny found that the stable form at the higher temp. has the m.p. 395°; E. Groschuff gave 396°; H. S. Roberts, 397·5°; and P. L. Robinson and co-workers gave 398·4°±0·5°. S. F. Schemtschuschny found that the m.p. diagram of mixtures of potassium chloride and dichromate has two branches meeting at the eutectic 366° and 27·5° molar per cent. of the chloride—Fig. 71. Solid soln. are formed only on the dichromate side of the curve, these contain about 25 molar per cent. of chloride. Sections viewed under the microscope have the uniform structure of solid soln. only when taken from the dichromate side of the eutectic, those on the chloride side show crystals of chloride embedded in the groundwork of the eutectic mixture. J. B. Robertson studied the equilibrium diagram for the system $Na_2Cr_2O_7 + 2KCl \rightleftharpoons K_2Cr_2O_7 + 2NaCl$ at 25°, 50°, and 100°; the results are plotted in Fig. 70. Potassium dichromate and sodium chloride are the compatible salt pair at all temp.; as the temp. increases the areas on the

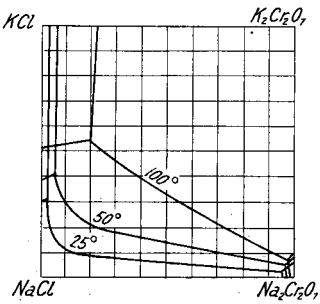


FIG. 70.—Reciprocal Salt Pair: $K_2Cr_2O_7 + 2NaCl = 2KCl + Na_2Cr_2O_7$.

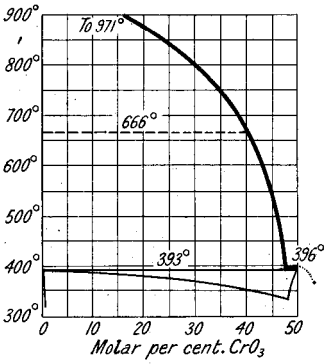


FIG. 71.—Freezing-point Curve of Mixtures of $K_2Cr_2O_7$–KCl.

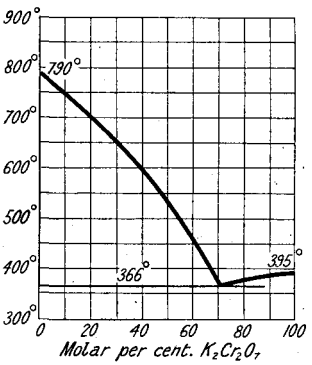


FIG. 72.—Freezing-point Curve of Mixtures of $KCrO_4$–$CrO_3$, or of $K_2Cr_2O_7$–$K_2CrO_4$.

diagram representing potassium and sodium chlorides increase considerably at the expense of the area representing potassium dichromate. The sodium dichromate

area is always very small. E. Groschuff found that the f.p. curve of mixtures of potassium chromate and dichromate falls regularly from the m.p. of the chromate at 971° to the eutectic at 393° and 99 per cent. of dichromate, and it then rises to 396° the m.p. of the dichromate. At the transition temp., $\alpha$-$K_2CrO_4 \rightleftharpoons \beta$-$K_2CrO_4$, 666°, the mixture contains about 75·5 per cent. of dichromate—Fig. 72. E. Groschuff's attempts to obtain the f.p. curve of mixtures of potassium chromate with over 50 molar per cent. of chromic acid were not successful owing to the decomposition of the chromic acid—Fig. 72. Potassium dichromate suffers considerable decomposition when heated to the m.p. of the monochromate. P. Grouvelle observed that at a high temp. potassium dichromate decomposes into potassium chromate, chromic oxide, and oxygen.

M. Amadori studied the m.p. of mixtures of potassium dichromate with the dimolybdate and the ditungstate. The f.p. of 0·5*M*- and 0·1*M*-$K_2Cr_2O_7$ is found by R. Abegg and A. T. Cox to be respectively —0·27° and —0·49°; I. Koppel and E. Blumenthal gave —0·63° for the f.p. of a sat. soln. having 4·5 grms. of salt per 100 grms. of water. This is the cryohydric or eutectic temp. for which F. Guthrie gave —0·7° with 0·18*M*-soln., and C. M. Guldberg, —0·8° with 0·15*M*-soln. M. S. Sherrill found the lowering of the f.p. of very dil. soln., and calculated the ionization factor $i$—**1**. 10, 15—to be :

| $K_2Cr_2O_7$ | 0·0005*M*- | 0·001*M*- | 0·00510*M*- | 0·1234*M*- | 0·02053*M*- |
|---|---|---|---|---|---|
| F.p. . | —0·00362° | —0·00706° | —0·0350° | —0·070° | —0·113° |
| $i$ . | 3·9 | 3·8 | 3·70 | 3·07 | 2·98 |

| $K_2Cr_2O_7$ . | 0·03004*M*- | 0·05340*M*- |
|---|---|---|
| F.p. . . | —0·158° | 0·263° |
| $i$ . . | 2·84 | 2·66 |

The first two sets of determinations quoted are by T. G. Bedford. The fact that the factor $i$ in dil. soln. approaches to 4 means that not only is the molecule $K_2Cr_2O_7$ ionized into three ions $K_2Cr_2O_7 \rightleftharpoons 2K^{\cdot} + Cr_2O_7''$, but that the acid residue is also hydrolyzed : $Cr_2O_7'' + H_2O \rightleftharpoons 2HCrO_4'$. H. G. Leopold and J. Johnston found the mol. lowering of the vap. press. of soln. containing 0·4, 0·6, and 1·0*M*-$K_2Cr_2O_7$ to be respectively 0·0498, 0·0472, and 0·0419. P. Kremers gave 104° for the b.p. of a sat. soln.; M. Alluard gave 103·4° at 718 mm. press.; and I. Koppel and E. Blumenthal, 104·8° for a soln. with 108 grms. of salt per 100 grms. of water. A. Speransky found that the vap. press., $p$ mm., of sat. soln. of the dichromate between 30·06° and 54·75° can be represented by $p = K\{(\theta - 77{\cdot}407)/\theta\}^{50}$, where $\log K = 7{\cdot}89408$. R. Lorenz and W. Herz studied some relations between the b.p. and the critical temp. W. Herz gave 29·8 Cals. for the heat of fusion per gram. J. G. F. Druce discussed the creeping of the salt during evaporation. M. Berthelot gave for the heat of formation, $(2H_2CrO_{4aq.}, 2KOH_{aq.}) = 27{\cdot}2$ Cals. at 8°; 26·8 Cals. at 12°; 26·4 Cals. at 18°; P. Sabatier gave 27·0 Cals. at 17°; and F. Morges, 24·982 Cals. at 19·5°. M. Berthelot also gave $(2CrO_{3aq.}, 2KOH_{aq.}) = 43{\cdot}8$ Cals. at 12°; and $(2CrO_{3solid}, 2KOH_{solid}) = 106{\cdot}8$ Cals. at 12°; $(2Cr(OH)_3, 2KOH_{aq.}, 3O) = K_2Cr_2O_{7aq.} + 37{\cdot}8$ Cals. at 8°, and with $K_2Cr_2O_{7solid}$, 54·8 Cals. at 8°; and with $KOH_{solid}$ and $K_2Cr_2O_{7solid}$, 113·0 Cals. at 8°; $(K_2CrO_{4solid}, CrO_{3solid}) = 15{\cdot}0$ Cals., and $K_2Cr_2O_7$(12 litres of water) + 4KOH(8 litres of water) $= 2K_2CrO_{4aq.} + 23{\cdot}6$ Cals. at 12°; while P. Sabatier gave 23·0 Cals. at 17°. H. Rose said that the dichromate dissolves in water with a feeble absorption of heat. For the heat of soln., T. Graham gave —17·08 Cals.; F. Morges gave for a mol of the salt in 825 mols of water —17·169 Cals. at 19·5°; J. Thomsen, with 400 mols. of water, —16·7 Cals. at 18°; and with 653·5 mols of water, M. Berthelot gave —17·02 Cals. at 11·6°, or —17·02–6($\theta$—15) Cals. at $\theta$°. E. von Stackelberg gave for a mol of $K_2Cr_2O_7$ at 17·5° with $n$ mols of water :

| $n$ . . . | ∞ | 1000 | 500 | 250 | 167 |
|---|---|---|---|---|---|
| Heat of solution | 18,400 | 17,440 | 16,885 | 16,335 | 16,000 cals. |
| Heat of dilution | 960 | 555 | 550 | 335 | |

DropDeads

H. Dufet gave for the indices of refraction of the triclinic crystals $\alpha=1{\cdot}7202$, $\beta=1{\cdot}7380$, and $\lambda=1{\cdot}8197$ for the Na-line; and $\beta=1{\cdot}7209$ for the Li-line; and P. L. Stedehouder and P. Terpstra gave for the pleochroic monoclinic crystals $\alpha=1{\cdot}715$, $\beta=1{\cdot}762$, and $\gamma=1{\cdot}892$. F. Fouqué found for the refractive indices, $\mu$, with the D-line with soln. of 5·9 grms. of $K_2Cr_2O_7$ in 1000 grms. of water:

| | 9·0° | 17·8° | 50·0° | 60·0° | 70·0° | 80·0° | 93·2° |
|---|---|---|---|---|---|---|---|
| $\mu$ . . | 1·3357 | 1·3350 | 1·3305 | 1·3289 | 1·3269 | 1·3259 | 1·3216 |

with soln. of 37·3 grms. $K_2Cr_2O_7$ per 1000 grms. of water:

| | 6·8° | 16·0° | 50·0° | 60·0° | 70·0° | 80·0° | 92·5° |
|---|---|---|---|---|---|---|---|
| $\mu$ . . | 1·3413 | 1·3405 | 1·3340 | 1·3340 | 1·3322 | 1·3300 | 1·3270 |

and with soln. of 89·2 grms. of $K_2Cr_2O_7$ per 1000 grms. of water:

| | 16·8° | 40·0° | 50·0° | 60·0° | 70·0° | 80·0° | 95·4° |
|---|---|---|---|---|---|---|---|
| $\mu$ . . | 1·3508 | 1·3476 | 1·3459 | 1·3441 | 1·3420 | 1·3397 | 1·3360 |

F. Flöttmann gave for soln. sat. at 15°, 20°, and 25° the values 1·35028, 1·35345, and 1·35685 for the D-line. J. Wagner, E. Viterbi and G. Krauz, A. Lallemand, E. Forster, K. Vierordt, P. Bary, B. K. Mukerji and co-workers, and R. L. Datta and N. R. Dhar made observations on this subject; and M. G. Mellon studied the colour of the soln. J. H. Gladstone gave for the equivalent refraction with the $\mu$-formula, 79·9. The extinction coeff. of 0·03399$M$-$K_2Cr_2O_7$ for light of wave-lengths $\lambda=508{\cdot}6\mu\mu$, $520{\cdot}9\mu\mu$, $536\mu\mu$, and $546{\cdot}1\mu\mu$ are respectively 2·12, 0·976, 0·246, and 0·117. L. R. Ingersoll found Verdet's constant for the **electromagnetic rotatary power** for light of wave-length 0·6, 0·8, 1·0, and 1·25$\mu$ to be 0·0108, 0·0064, 0·0042, and 0·0025 respectively for soln. of sp. gr. 1·085. The **absorption spectrum** was studied by P. Sabatier, A. Étard, O. Knoblauch, F. Grünbaum, K. S. Gibson, H. C. Jones and W. W. Strong, T. Aden, N. R. Tawde and G. R. Paranjpe, G. Jander, J. Formanek, W. Böhlendorff, H. Bremer, F. Melde, G. Rössler, J. Müller, J. M. Hiebendaal, H. Settegast, and C. P. Smyth. I. Plotnikoff and M. Karsulin observed that the absorption of light by potassium dichromate begins at $595\mu\mu$, and extends towards the ultra-violet. The photochemical absorption begins at $595\mu\mu$ in the yellow, reaches a maximum at $500\mu\mu$ in the green, and then decreases to about $240\mu\mu$. According to C. Schaefer and M. Schubert, the ultra-red reflection spectrum of potassium dichromate has three maxima, one at 18·12$\mu$, and complex ones at 12·14$\mu$ to 13·22$\mu$, and at 10·44$\mu$ to 11·1$\mu$. A. E. Lindh, D. Coster, and O. Stelling studied the **X-ray spectra**. H. von Halban and K. Siedentopf, and J. B. Ferguson discussed the potassium dichromate and molybdenum nitrate light filter. H. M. Vernon estimated the degree of ionization of aq. soln. of the salt from the colour. I. Plotnikoff, and M. Schwarz studied the photochemical oxidation of organic compounds by dichromates and chromates—*vide supra*, chromium trioxide. A. Reychler observed that in darkness there is no perceptible action between potassium iodide, and dichromate, and eosin in aq. soln., but in light iodine is liberated. A. Kailan found that an aq. soln. of potassium dichromate is reduced at the rate of $3\times10^{11}$ mol per second by exposure to radium rays. R. Hunt thought that actinized soln. of potassium dichromate produce precipitates of chromates of a different colour from those obtained from soln. made and kept in the dark. F. Bush showed that the difference is due to the difference in the rate of mixing the soln., and not an effect of actinization—*vide supra*, silver chromate. T. Svensson studied the change in the conductivity, and potential of soln. of potassium dichromate in sulphuric acid when exposed to light. W. Herz gave $2{\cdot}42\times10^{12}$ for the vibration frequency. A. Kailan found that the salt is decomposed by exposure to radium radiations. E. Montignie observed that potassium dichromate, after exposure to ultra-violet light, affects a photographic plate.

J. A. Fleming and J. Dewar found that the dielectric constant of water with some potassium dichromate in soln. is not much affected, and similarly at −185°.

W. Schneider observed no piezoelectric effect. R. Lorenz and H. T. Kalmus found the sp. electrical conductivity of the fused salt to be:

| | 397° | 417° | 437° | 457° | 477° | 497° | 507° |
|---|---|---|---|---|---|---|---|
| Sp. cond. . | 0·1959 | 0·2381 | 0·2745 | 0·3109 | 0·3473 | 0·3837 | 0·4019 mho. |

Observations on the conductivity of aq. soln. were made by R. Lenz, M. S. Sherrill, P. Walden, and J. Lundberg. A. Heydweiller found for 0·1*N*-, 0·2*N*-, and 0·5*N*-soln., the respective values 0·01010, 0·02012, and 0·05005 for the sp. gr. at 18°, and 98·2, 93·1, and 85·4 for the eq. electrical conductivities. H. C. Jones and C. A. Jacobson observed the mol. conductivity, $\mu$ mho, between 0° and 35°, and A. P. West and H. C. Jones between 35° and 65° when a mol of the salt is dissolved in $v$ litres:

| $v$ | | 8 | 16 | 32 | 128 | 512 | 1024 | 2048 |
|---|---|---|---|---|---|---|---|---|
| $\mu$ | 0° | 116·3 | 128·7 | 137·5 | 152·6 | 190·6 | 204·9 | 214·6 |
| | 10° | 153·7 | 171·1 | 184·2 | 204·5 | 260·8 | 280·5 | 294·3 |
| | 25° | 216·9 | 243·0 | 262·9 | 297·0 | 384·0 | 420·5 | 441·7 |
| | 35° | 261·7 | 294·5 | 319·9 | 365·3 | 475·4 | 522·8 | 553·4 |
| | 65° | 352·9 | — | 396·9 | 417·9 | 426·8 | — | 448·9 |
| $\alpha$ | 0° | 54·2 | 60·0 | 64·1 | 71·1 | 88·8 | 95·5 | 100·0 |
| | 35° | 47·3 | 53·2 | 57·8 | 66·0 | 85·9 | 94·5 | 100·0 |
| | 65° | 78·6 | — | 88·4 | 93·1 | 95·1 | — | 100·0 |

The calculated values for the percentage ionization, $\alpha$, are also indicated. W. C. D. Whetham gave for the eq. conductivity, $\lambda$ mho, with soln. containing $N$-gram-equivalents per litre at 0°:

| $N$ | 0·00001 | 0·0001 | 0·001 | 0·01 | 0·1 | 0·2 |
|---|---|---|---|---|---|---|
| $\lambda$ | 81·3 | 76·3 | 71·4 | 70·4 | 64·3 | 61·5 |

and inferred from the small rise in conductivity with increasing dilution soln. of medium conc., and a larger change with soln. of small conc., that in the former case the ionization proceeds $Cr_2O_7'' + H_2O \rightleftharpoons 2HCrO_4'$, and in the latter case $HCrO_4' \rightleftharpoons H^{\cdot} + CrO_4''$. E. Spitalsky found the $H^{\cdot}$-ion conc., from observations on the effect of the dichromate soln. on the velocity of hydrolysis of diazoacetic ether, to be 0·000259 with soln. containing 0·1012 mol of $K_2Cr_2O_7$ per litre, and 0·000188 with soln. containing 0·0664 mol per litre. W. V. Bhagwat and N. R. Dhar found that the salt exists in aq. soln. probably as $KHCr_2O_4$. G. P. Vincent studied the depolarizing action of acidic soln. of the dichromate on hydrogen liberated at a smooth platinum electrode. T. Murayasu studied the conductivity of soln. in glycine. W. Spring observed that soln. of dichromate, on standing, slowly change their colour, and their electrical conductivity; this means that there is a slow change in the condition of the soln.—*vide supra*, potassium chromate, and chromic acid. H. Buff observed that on electrolysis of the molten salt, oxygen is evolved at the anode; and F. Morges added that the dichromate is reduced to chromate at the cathode—*vide supra*. For the photochemical action of light, *vide* chromic acid. S. Schlivitch observed a photovoltaic effect with soln. of potassium dichromate and platinum electrodes. F. Weigert studied the electrolytic reduction of soln. of the dichromate. J. B. Johnson discussed the e.m.f. due to the thermal agitation of a soln. of the dichromate.

G. Meslin said that potassium dichromate is paramagnetic. He found that the magnetic susceptibility of the powder is $0{\cdot}13 \times 10^{-6}$ mass unit; and G. Quincke gave for a soln. of the dichromate between 18° and 20°, $0{\cdot}76 \times 10^{-6}$ mass unit. J. Forrest measured the variations in the parallel and transverse components of the magnetization of the crystals. P. Weiss and P. Collet found the paramagnetism of a soln. of the dichromate is constant between 14° and 50°; and the subject was discussed by P. Weiss, L. A. Welo and A. Baudisch, and S. Berkman and H. Zocher. W. G. Hankel and H. Lindenberg found that the crystals exhibit pyroelectricity in that when warmed the (001)-face is usually positively electrified, and the $(00\bar{1})$-face negatively electrified—the reverse behaviour is rare.

T. Thomson said that potassium dichromate has a cooling, bitter, metallic taste; it is stable in air, and is not hygroscopic. V. Ipatieff and A. Kisseleff found that when $2N$-$K_2Cr_2O_7$ with some conc. sulphuric acid is exposed to hydrogen at 180° to 200 atm. press., a crystalline compound, $K_2O.Cr_2O_3.Cr_2(SO_4)_3.H_2O$, is formed. It is insoluble in acid, and is dissolved by molten sodium carbonate and potassium nitrate. H. P. Cady and R. Taft found potassium dichromate to be appreciably soluble in phosphoryl chloride, and very slightly soluble in liquid sulphur dioxide. According to C. F. Cross, in an atm. sat. with moisture, a mol of the salt takes up 3·5 mols of water which is removed by pressing it between filter-papers. Observations on the solubility of potassium dichromate in water were made by T. Thomson, H. Moser, M. le Blanc, M. Alluard, P. Kremers, M. S. Sherrill, A. Michel and L. Krafft, and H. G. Greenish and F. A. U. Smith. The following observations on the percentage solubility, $S$, are due to I. Koppel and E. Blumenthal for temp. below 100°, and to W. A. Tilden and W. A. Shenstone for temp. above 110°:

| | −0·63° | 0° | 30° | 60° | 104·8° | 117° | 148° | 180° |
|---|---|---|---|---|---|---|---|---|
| $S$ | 4·31 | 4·43 | 15·40 | 31·30 | 52·00 | 56·10 | 66·80 | 72·50 |

—*vide* Figs. 36 to 41. F. A. H. Schreinemakers gave 18·12 per cent. at 30°. A. Étard obtained the following values for $S$:

| | 1° | 20° | 61° | 104° | 150° | 215° | 312° | 360° |
|---|---|---|---|---|---|---|---|---|
| $S$ | 4·1 | 10·4 | 30·2 | 48 | 60·8 | 76·9 | 91·8 | 97·4 |

but the results are considered to be too low. F. Flöttmann found the solubility at 15°, 20°, and 25° to be 0·321, 0·396, and 0·482 mols per litre, or 8·893, 10·822, and 12·980 per cent. R. Marc, M. le Blanc and W. Schmandt, and E. V. Murphree measured the rate of soln. of the salt in water, and showed that the process is determined by the rate of diffusion of the salt from the surface of the solid into the body of the liquid. J. Traube and W. von Behren discussed the formation of submicrons during the dissolution of the dichromate. T. Thomson said that an aq. soln. of the salt reddens litmus, and R. T. Thomson, and J. A. Wilson, that it is neutral towards lacmoid. The hydrolysis, $Cr_2O_7'' + H_2O \rightleftharpoons 2CrO_4'' + 2H^{\cdot}$, was studied by J. Sand and K. Kästle, and the equilibrium constant, $K=[CrO_4'']^2[H^{\cdot}]^2/[Cr_2O_7'']$, could not be determined satisfactorily owing to unrecognized disturbing conditions, but approximate estimates gave $K=1{\cdot}5\times10^{-13}$ at 25°; consequently, a 0·1$N$-soln. is 0·18 per cent. hydrolyzed. W. Herz and F. Hiebenthal gave for the solubility of potassium dichromate, $S$, one-sixth mol per litre, in $n$-normal soln. of lithium chloride, etc.:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| LiCl | $n$ | 0 | 0·49 | 0·92 | 1·78 | 2·78 | 3·61 | 4·49 |
| | $S$ | 2·89 | 2·78 | 2·55 | 2·26 | 1·85 | 1·37 | 1·32 |
| NaCl | $n$ | 0·47 | 0·94 | 1·91 | 2·84 | 3·80 | 4·21 | 5·63 |
| | $S$ | 2·91 | 2·98 | 2·79 | 2·62 | 2·33 | 2·24 | 2·06 |
| $NH_4Cl$ | $n$ | 0·73 | 1·79 | 2·59 | 3·10 | 4·00 | 5·32 | |
| | $S$ | 2·82 | 2·54 | 2·32 | 2·16 | 1·83 | 0·91 | |
| $MgCl_2$ | $n$ | 0·45 | 0·93 | 1·84 | 2·31 | 2·74 | 3·15 | |
| | $S$ | 2·78 | 2·64 | 2·24 | 2·07 | 1·91 | 1·76 | |
| $CaCl_2$ | $n$ | 0·24 | 0·45 | 0·92 | 1·41 | 1·64 | 1·87 | 11·42 |
| | $S$ | 2·88 | 2·91 | 2·84 | 2·69 | 2·62 | 2·56 | 1·88 |
| $SrCl_2$ | $n$ | 0·51 | 1·00 | 2·02 | 2·28 | 2·84 | 3·47 | |
| | $S$ | 2·89 | 2·91 | 2·73 | 2·69 | 2·62 | 2·38 | |

where for LiCl, $S=2{\cdot}90-0{\cdot}352n$; for NaCl, $S=3{\cdot}195-0{\cdot}230n$; for $NH_4Cl$, $S=3{\cdot}066-0{\cdot}309n$; for $MgCl_2$, $S=2{\cdot}95-0{\cdot}380n$; for $CaCl_2$, $S=3{\cdot}02-0{\cdot}250n$; and for $SrCl_2$, $S=3{\cdot}12-0{\cdot}210n$.

A. C. Robertson represented the catalytic action of the dichromate on hydrogen dioxide by the cyclic reactions: $K_2Cr_2O_7+H_2O_2=2KCrO_4+H_2O$, and $2KCrO_4+H_2O_2=K_2Cr_2O_7+H_2O+O_2$. E. Pietsch and co-workers studied the surface-conditions in the reaction between potassium dichromate and hydrogen dioxide. For the action of hydrogen dioxide, *vide infra*, perchromates. J. W. Thomas

found that potassium dichromate first forms potassium chloride, and chromium trioxide, and then a brown chromium oxide, but no chromyl chloride.

W. K. van Haagen and E. F. Smith found that hydrogen fluoride passed over heated potassium dichromate removes nearly all the chromium. According to F. Fichter and E. Brunner, if a dil. soln. of potassium dichromate is treated with fluorine, it becomes green and is reduced to a chromic salt, most probably the fluoride. Crude fluorine always containing free hydrogen fluoride; the action of fluorine upon an aq. soln. furnishes hydrofluoric acid and its conc. may be sufficient for the formation of chromic fluoride. In this case, fluorine acts as a reducing agent. This contradictory behaviour must be explained by the intermediate formation of hydrogen dioxide, thus: $2H_2O+F_2=H_2O_2+2HF$. The formation of hydrogen dioxide can be detected by working with a small quantity of chromic acid and in the presence of dil. sulphuric acid; under these conditions and by proper cooling we obtain the blue perchromic acid, soluble in ether. Perchromic acid is very unstable, losing oxygen and yielding chromic salts; in this manner the reduction of dichromate can be carried out quantitatively by prolonged treatment with fluorine. K. H. Butler and D. McIntosh observed that the dichromate is insoluble in liquid chlorine, and has no action on the b.p. of the liquid. According to E. M. Péligot, a soln. of potassium dichromate in boiling hydrochloric acid deposits, on cooling, potassium chlorochromate. R. E de Lury, and G. Kernot and F. Pietrofesa concluded from their observations on the action of potassium dichromate on acidic soln. of iodides that the reaction is of the first order with respect to the $Cr_2O_7''$-ion, nearly of the second order with respect to the $H^{\cdot}$-ion, and between the first and second order with respect to the $I'$-ion. R. F. Beard and N. W. Taylor showed that there are many anomalous results in connection with the reaction: $Cr_2O_7''+6I'+14H^{\cdot}=2Cr^{\cdot\cdot\cdot}+7H_2O+3I_2$, which disappear in the presence of 1·5*M*-NaCl. Two simultaneous reactions occur: $H^{\cdot}+I'+Cr_2O_7''\rightarrow HI.Cr_2O_7''$; and $2H^{\cdot}+2I'+Cr_2O_7''\rightarrow(HI)_2.Cr_2O_7''$. The velocity constant, $k$, is given by $k=14{\cdot}6[H^{\cdot}][I']+53000[H^{\cdot}]^2[I']^2$. The reaction was studied by N. A. Izgarischeff and A. K. Belaieff.

J. B. Senderens found that a soln. of potassium dichromate is decolorized by boiling it with sulphur, forming $Cr_7O_{12}$, or $3Cr_2O_3.CrO_3$, and a soln. of potassium sulphate and thiosulphate. A. Manuelli found that if a mixture of sulphur and the dichromate is heated in a sealed tube, chromic oxide is formed; and K. Brückner said that the reaction of the dichromate resembles that of the monochromate (*q.v.*) with sulphur—*vide supra*, the preparation of chromic oxide. A. A. Hayes said that hydrogen sulphide precipitates some hydrated chromic oxide mixed with sulphur; and P. Berthier, that sulphur dioxide colours the soln. green forming potassium chromic sulphate and dithionate. H. Bassett said that 94–95 per cent. of chromic sulphate and 5–6 per cent. of dithionate are formed. W. R. Hodgkinson and J. Young studied the action of dry sulphur dioxide on the salt. O. Popp represented the reaction with sodium thiosulphate: $2K_2Cr_2O_7+Na_2S_2O_3=K_2CrO_4+Cr_2O_3.CrO_3+K_2SO_4+Na_2SO_3$. W. H. Balmain found that when 3 parts of the dichromate are heated with 4 parts of sulphuric acid, chromium and potassium sulphates, water, and oxygen are formed, and he used this mode of preparing oxygen in preference to the potassium chlorate process—*vide supra*, chromium trioxide. G. Grather and T. Nagahama observed that potassium dichromate is reduced by sodium sulphide, sulphite, and thiosulphate in the order of increasing effect. M. Traube found that a mol of the salt dissolved in 3·5 parts of water and treated with 2 mols of $H_2SO_4$ in the cold is not decomposed, but it is decomposed by 3 mols of sulphuric acid with 0·5 part of water per mol of salt, but not with 2 parts of water. H. Schwarz made observations on this subject—*vide supra*, the preparation of chromium trioxide. E. C. Franklin and C. A. Kraus found that the salt is insoluble in liquid ammonia. The action of ammonium chloride has been indicated in connection with the preparation of chromic oxide. F. Santi found that a conc. soln. of ammonium chloride may convert the dichromate to chromic

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acid. According to G. B. Frankforter and co-workers, the reaction which takes place when the mixture is heated at 290° is different from that which occurs at a dull red-heat, the composition of the gas evolved and of the residue left after lixiviation being different in the two cases. A mixture of ammonium chloride and potassium dichromate does not undergo any change until a temp. of 210° is attained. The mixture then becomes yellowish-brown, owing to the formation of chromium dioxide. At 260°, a slate-coloured residue is obtained, which, on lixiviation with water, leaves small, greenish-black, iridescent spangles of a hydrated chromium oxide, $Cr_2O_3.2H_2O$. The change which takes place does not depend only on the temp., but also on the proportions of the salts employed. At 370°, in presence of a considerable excess of ammonium chloride, chromium chloride and ammonia are formed. If, however, the potassium dichromate is in large excess, a black residue is obtained, together with some unchanged dichromate. Under certain conditions, chlorine is liberated, and in some cases, a nitride of chromium is produced. It is supposed that the complexity of the reaction is largely due to the dissociation of ammonium chloride, which is the first change to take place when the mixture is heated. E. Mitscherlich, and F. Bothe found that a soln. of the salt in nitric acid deposits crystals of the terchromate. E. Kopp said that phosphorus reduces the soln. in sunlight or when heated, forming potassium chromate and a little chromium phosphate. A. Michaelis found that in a sealed tube, the salt is partially decomposed phosphorus trichloride at 166°, forming potassium chlorochromate, phosphoryl chloride, potassium phosphate, and chromium chromate. A mixture with carbon detonates slightly when heated. S. Levites studied the adsorption of the salt from aq. soln. by charcoal. E. J. Bowen and C. W. Bunn studied the photochemical oxidation of alcohols by dichromates. H. B. Weiser and E. B. Middleton attributed the conversion of potassium dichromate into chromate, observed by N. Ishizaka, to the disturbance of the equilibrium : $Cr_2O_7'' + H_2O \rightleftharpoons 2H^{\cdot} + 2CrO_4'$, by the preferential adsorption of $H^{\cdot}$-ions by the alumina. W. Kuczynsky found that a 4 per cent. soln. of potassium dichromate electrolytically pitted the surface of aluminium at 220 volts. J. Morland, and A. Reinecke studied the action of ammonium thiocyanate. B. Reinitzer found that the dichromate is insoluble in alcohol. E. J. Bowen and E. T. Yarnold studied the photochemical oxidation of ethyl alcohol by the dichromate. L. Godefroy studied the joint action of alcohol and chlorine or iodine; and A. Commaille, the joint action of acids and ether. F. W. O. de Coninck observed that 100 grms. of a sat. soln. in glycol contain 6 grms. of potassium dichromate. A. Naumann found that the salt is insoluble in benzonitrile, and acetone; and W. Eidmann, insoluble in acetone and methylal. D. Lindo observed that a brown colour is produced with phenol, and E. A. Parnell studied the joint action of phenol and hydrogen dioxide. J. Piccard and F. de Montmollin observed that the oxidation of aniline by potassium dichromate is a reaction of the second order. A. Commaille found that tannin gives a brown precipitate. For the action on gelatin, *vide supra*, chromic acid. G. Grather and T. Nagahama studied the reduction of dichromates to basic chromates by lactic acid, tartaric acid, glucose, dextrose, tannin, glycerol, formaldehyde, thiosulphates, sulphites, and sulphides, and found that the relative activity of these substances decreases in the order given. Methyl alcohol did not reduce the salt. J. W. Williams and E. M. Drissen investigated the action of the salt on cysteine. E. H. Riesenfeld and O. Hecht studied the photochemical reaction with ethylene glycol; and J. Plotnikoff, and D. S. Morton, the photoxidation of organic compounds by the dichromate.

S. Kern represented the reaction with magnesium : $K_2Cr_2O_7 + Mg + 2H_2O = MgCr_2O_7 + 2KOH + H_2$; and E. Heyn and O. Bauer observed that a dil. soln. of the dichromate dissolves iron, but soln. of certain concentrations retard the rusting of iron. W. P. Jorissen and G. M. A. Kayser discussed the reaction with sulphur and aluminium, and sulphur and iron. According to F. Margueritte, dil. soln. of potassium dichromate become paler in colour when treated with potassium chloride, nitrate, or sulphur, with ammonium nitrate or sulphate, or with sodium carbonate or

tetraborate. H. J. P. Venn and V. Edge noted that basic cupric chlorides are formed by the action of a dil. soln. of potassium dichromate on cuprous chloride. When the dichromate is mixed with silicon and heated in the electric arc, L. Kahlenberg and W. J. Trautmann found that it is readily reduced to a porous green slag. J. C. Witt, and M. Neidle and J. C. Witt, studied the action of potassium dichromate on stannous sulphate and stannous chloride. According to E. R. Bullock, the reaction between silver in gelatin and a soln. containing potassium dichromate and a bromide, slightly acidified with acetic acid, only occurs in presence of potassium ferricyanide or copper sulphate, which appear to act as catalysts. The action of the catalyst is attributed to the greater simplicity of the initial ionic reaction: $Fe(CN)_6'''+Ag=Ag^{\cdot}+Fe(CN)_6''''$, or $Ag+Cu^{\cdot\cdot}=Ag^{\cdot}+Cu^{\cdot}$, as compared with $3Ag+Cr^{\cdot\cdot\cdot\cdot\cdot\cdot}=3Ag^{\cdot}+Cr^{\cdot\cdot\cdot}$, which involves four ions instead of two. The concentrated soln. of potassium dichromate in 0·3*N*-NaOH increases up to 6·5 per cent. when shaken with animal charcoal—negative adsorption; with more dil. soln., the conc. is diminished—positive adsorption. The negative adsorption is explained on the assumption that the conc. of the water on the surface of the particles of charcoal is increased. E. Brentel recommended potassium dichromate as a standard for acidimetry. R. G. van Name and F. Fenwick studied the electrometric titration of ferrous salts with potassium dichromate; K. Someya, the action of potassium dichromate on potassium ferrocyanide; and M. M. Narkevich, the acceleration due to oxidation produced by the dichromate when copper dissolves in sulphuric acid.

W. K. Sullivan added that if an almost boiling soln. of a mol of potassium dichromate is treated with 2 mols of sulphuric acid, the orange-red crystals which separate on cooling appear to be *potassium dihydrosulphatodichromate* because they have the composition $K_2Cr_2O_7.2KHSO_4$, but there is really nothing to show that this is a chemical individual. According to J. Fritzsche, *potassium disulphodichromate*, $K_2(Cr,S)_2O_7$, or $KO.SO_2.O.CrO_2.OK$, is formed in the preparation of chromic acid by the action of sulphuric acid on an excess of potassium dichromate. H. Reinsch, and H. Schiff, however, regarded the product so obtained as a mixture of potassium sulphate and dichromate. H. Schiff represented the action of fused potassium chlorochromate on potassium sulphate by the equation: $K_2SO_4+KCrO_3Cl=KCl+KO.CrO_2.O.SO_2.OK$; and on potassium hydrosulphate, by: $KHSO_4+KCrO_3Cl=HCl+KO.CrO_2.O.SO_2.OK$. He said that the colour of the salt is the same as that of potassium dichromate; and that it is decomposed by water into potassium sulphate and dichromate, and sulphuric acid.

L. Grandeau [5] prepared crystals of **rubidium dichromate,** $Rb_2Cr_2O_7$, from a soln. of rubidium carbonate in an excess of a warm aq. soln. of chromic acid. F. A. H. Schreinemakers and A. Filippo's observations on the equilibrium conditions are summarized in Fig. 46. According to G. N. Wyrouboff, there are three forms, a monoclinic form and two triclinic forms, but observations by J. A. le Bel, W. Stortenbecker, and B. Gossner have established the existence of only two varieties—monoclinic and triclinic. W. Stortenbecker said that the monoclinic form is alone produced when soln. are crystallized below 35°, and the triclinic form when crystallization occurs at temp. above 75°; and J. A. le Bel said that the red triclinic variety alone crystallizes from acidic soln., whilst in the presence of a little alkali, the yellow monoclinic modification separates. The dimorphism is not conditioned by temp. alone. W. Stortenbecker added that the monoclinic and triclinic modifications of rubidium dichromate are monotropic, but that the small difference in stability between them retards the transformation of one into the other. If the time is great, the triclinic form is obtained, but a rapid crystallization gives sometimes the monoclinic, sometimes the triclinic, and sometimes a mixture of the two. This is probably the explanation of G. N. Wyrouboff's statement to the effect that, if crystals of one form are placed in contact with a sat. soln. of the other, they remain indefinitely without showing the slightest indication of transformation, no matter what the temp. G. N. Wyrouboff gave for the axial ratios of the monoclinic crystals $a:b:c=0·596:1:0·3388$, and $\beta=87°\ 8'$; while B. Gossner gave $1·0202:1:1·8081$, and $\beta=93°\ 28·5'$. G. N. Wyrouboff found that the (010)-cleavage is incomplete, that the optic axial angle $2V=83°\ 16'$; the optical character is negative; and the sp. gr. is 3·021.

The axial ratios of the triclinic pinacoids are $a:b:c=0{\cdot}5609:1:0{\cdot}5690$, and $\alpha=91°\,0'$, $\beta=93°\ 52'$, and $\gamma=81°\ 34'$. B. Gossner said that the (001)- and (010)-cleavages are complete, and that the (100)-cleavage is distinct. G. N. Wyrouboff found that the optical axial angle $2E=107°\ 42'$; the optical character is positive; and the sp. gr. is 3·125. A. F. Hallimond discussed the mol. vols. of the isomorphous dichromates. The monoclinic form is considered by W. Stortenbecker to be the labile form more easily soluble in water; and he gave for the solubility, $S$ per cent.:

| | | (14°) | 18° | (26°) | 30° | 40° | (43°) | 50° | 65° |
|---|---|---|---|---|---|---|---|---|---|
| $S$ | monoclinic | 4·45 | 5·42 | 8·00 | 9·08 | 13·22 | 16·52 | 18·94 | 28·8 |
| | triclinic | 4·40 | 4·96 | 7·91 | 8·70 | 12·90 | 14·57 | 18·77 | 27·3 |

The data for the bracketed temp. were determined by G. N. Wyrouboff. According to J. A. le Bel, a red crystal placed in a soln. from which yellow crystals are separating passes into soln. so that the solubility of the two forms is not the same. F. A. H. Schreinemakers and A. Fillippo found that a sat. soln. contains 9·47 per cent. $Rb_2Cr_2O_7$ at 30°.

According to C. Chabrié,[6] the evaporation of an aq. soln. of 100 parts of cæsium chromate and 26 parts of chromium trioxide furnishes **cæsium dichromate,** $Cs_2Cr_2O_7$; F. R. Fraprie obtained the salt by treating cæsium chromate with sulphuric acid. The conditions of equilibrium worked out by F. A. H. Schreinemakers and D. J. Meijeringh are summarized in Fig. 47. C. Chabrié said that the pale red crystals are very stable; and F. R. Fraprie added that the crystals are triclinic with complete basal cleavage; and they are much more soluble in hot than in cold water. A. F. Hallimond discussed the mol. vols. of the isomorphous dichromates. F. A. H. Schreinemakers and D. J. Meijerinck represented for the solubilities of the different alkali dichromates, at 30°,

| | Li | Na | $NH_4$ | K | Rb | Cs |
|---|---|---|---|---|---|---|
| $M_2Cr_2O_7$ | 56·6 | 66·4 | 32·05 | 15·34 | 9·47 | 5·20 |

F. Dröge,[7] J. Schulze, and M. Gröger prepared **cupric dichromate,** $CuCr_2O_7.2H_2O$, by evaporating a soln. of cupric hydroxide in aq. chromic acid, and, if any green crystals separate, pouring off the clear soln., and evaporating the remaining liquor over conc. sulphuric acid. C. Freese obtained a basic chromate by this process. L. Balbiano obtained cupric dichromate by evaporating a soln. of the basic chromate in aq. chromic acid—if alcohol is added to the soln., a basic chromate is precipitated. A. Viefhaus obtained cupric dichromate from the soln. obtained by treating barium chromate with cupric sulphate, and J. Schulze, from the soln. of cupric carbonate in aq. chromic acid. F. Zambonini said that the triclinic crystals have the axial ratios $a:b:c=0{\cdot}6133:1:0{\cdot}5117$, and $\alpha=67°\ 2'\ 16''$, $\beta=125°\ 14'\ 3''$, and $\gamma=111°\ 26'\ 2''$; and the sp. gr. is 2·286 at 19°. F. Dröge, and J. Schulze said that the crystals of the dichromate are brownish-black; they lose all their water at 100°, and decompose at a red-heat; they deliquesce in air; are sparingly soluble in water without decomposition; they are also soluble in alcohol, and in aq. ammonia. N. Parravano and A. Pasta obtained cupric tetramminodichromate, $CuCr_2O_7.4NH_3.2H_2O$, in black prismatic crystals by evaporating an ammoniacal soln. of the compound which cupric dichromate forms with pyridine. J. Schulze said that if a soln. of cupric dichromate be treated with an excess of cupric carbonate, the basic product has a variable composition. A. and L. Lumière and A. Seyewetz observed that light reduces cupric dichromate gelatine less readily than gelatine with ammonium dichromate. N. Parravano and A. Pasta obtained complex salts with pyridine, aniline, and ethylenediamine. G. Krüss and O. Unger prepared **ammonium cupric dichromate,** $3(NH_4)_2Cr_2O_7.2CuCr_2O_7.6H_2O$, in dark brown tetragonal crystals, by evaporating or cooling a hot conc. soln. of 2 molar parts of ammonium dichromate and cupric dichromate. It loses its water, with some decomposition, at 100°; and at a higher temp., it decomposes with incandescence. The salt is soluble in water. A. Stanley reported **sodium copper dioxydichromate,**

$Na_2Cr_2O_7.2CuO.CuCr_2O_7.4H_2O$, by the action of a soln. of sodium dichromate on freshly-precipitated cupric hydroxide. The brown, microcrystalline powder loses water at 200°, and decomposes at a higher temp. It is almost insoluble in water; and only slightly soluble in alcohol.

According to H. Moser,[8] the action of chromic acid on a soln. of silver nitrate furnishes ruby-red crystals of **silver dichromate,** $Ag_2Cr_2O_7$; L. N. Vauquelin obtained the same salt from a soln. of silver chromate and nitric acid. O. Mayer, and W. Autenrieth used similar processes. R. Warington, C. Freese, W. Autenrieth, and E. Jäger and G. Krüss obtained the salt by adding potassium dichromate to a soln. of silver nitrate. A. Janek, and M. S. Dunin and F. M. Shemyakin studied the formation of rhythmic rings of silver dichromate. G. P. Baxter and R. H. Jess mixed potassium dichromate or chromic acid and silver nitrate in nitric acid, and crystallized silver dichromate from 0·16*N*- to 3*N*-$HNO_3$, and dried the product at 150°, and afterwards powdered the product and dried it at 200° in a current of dry air. E. R. Riegel and M. C. Reinhard, D. A. Audalian, E. S. Hedges, and E. S. Hedges and R. V. Henley studied the formation of rhythmic rings of silver dichromate in gelatine—*vide supra*, silver chromate. R. Warington, and A. Helmsauer found that a silver plate becomes covered with scarlet crystals of silver dichromate when it is immersed in a soln. of potassium chromate and dichromate and sulphuric acid—a little chromic oxide is formed. G. H. Zeller said that heat hastens the formation of the crystals. The crystals appear dark brown or dark grey or black in reflected light, and scarlet-red or carmine-red in transmitted light. J. Schabus said that the triclinic pinacoids have the axial ratios $a:b:c=1{\cdot}5320:1:1{\cdot}0546$. H. G. F. Schröder found the sp. gr. to be 4·669; while G. P. Baxter and R. H. Jess gave 4·770 at 25°/4°. R. Warington found the dichromate to be sparingly soluble in water forming a bright yellow soln. which reddens litmus, and yields crystals on evaporation. When boiled with water, it forms dark green chromate, and an acidic soln. which deposits the dichromate on cooling; W. Autenrieth represented the reaction $Ag_2Cr_2O_7+H_2O=Ag_2CrO_4+H_2CrO_4$. O. Mayer gave for the solubility $1{\cdot}9\times10^{-4}$ mol per litre at 15°; and M. S. Sherrill and D. E. Russ, $7{\cdot}3\times10^{-3}$ mol per litre at 25°. M. S. Sherrill and D. E. Russ said that water, and nitric acid below 0·06*N*-$HNO_3$, decompose the dichromate with the separation of chromate. They found for the solubility, *S* milliatoms per litre, at 25°:

| | $HNO_3$ . | 0*N*- | 0·01*N*- | 0·02*N*- | 0·04*N*- | 0·06*N*- | 0·08*N*- | 0·10*N*- |
|---|---|---|---|---|---|---|---|---|
| *S* | Cr . | 32·20 | 25·06 | 20·21 | 13·59 | 11·10 | 11·10 | 0·624 |
| | Ag . | 5·390 | 6·131 | 7·148 | 9·529 | 11·10 | 11·10 | — |
| Solid phase. | | $Ag_2CrO_4+Ag_2Cr_2O_7$ | | | | $Ag_2Cr_2O_7$ | | |

R. Warington said that the salt is freely soluble in nitric acid and in aq. ammonia. A. Helmsauer said that when heated to redness, silver, and chromic oxide are formed. F. B. Hofmann observed that the powdered dichromate collects at the boundary surface when shaken with a mixture of water and benzene, toluene, xylene, or chloroform. S. H. C. Briggs observed the formation of complex salts with pyridine, $Ag_2Cr_2O_7.4(\text{and }6)C_5H_5N$; and G. Krüss, and S. Darby, complex salts—$Ag_2Cr_2O_7.1(\text{and }2)HgCy_2$. R. G. van Name and R. S. Bothworth found that when silver sulphate and dichromate, the former greatly in excess (99 : 1), are crystallized at a temp. of 25° from an acidic soln. (standard soln. of sulphuric acid), there are obtained solid soln. of sulphate and dichromate, ranging in colour from pale yellow to scarlet, and with the same rhombic form as the pure sulphate. These crystals contain up to 4·1 molar per cent. of dichromate. When a greater proportion of dichromate is present in the acidic soln., crystals of the dichromate alone separate. J. W. Retgers could not prepare solid soln. of these two salts. P. Ray and J. Dasgupta studied complexes with hexamethylenetetramine.

L. N. Vauquelin[9] prepared **calcium dichromate,** $CaCr_2O_7.3H_2O$, from a soln. of calcium oxide in chromic acid; and J. F. Bahr, from a soln. of calcium chromate

in chromic acid, and evaporating the liquor over conc. sulphuric acid, or in vacuo. F. Mylius and J. von Wrochem supposed that the salt is tetrahydrated, but they obtained the dichromate, in red, six-sided plates, from a sat. soln. at 18°, when 61 per cent. of $CaCr_2O_7$ is present. When freshly prepared, the crystals of the trihydrate are red, but when left on a porous tile in a desiccator, they become yellowish-brown. They lose water when heated; and at a higher temp. they melt to a reddish-brown liquid. K. S. Nargund and H. E. Watson observed that calcium dichromate gives off oxygen at 250° in vacuo, and decomposes at 500° into calcium chromate and chromic oxide. Calcium dichromate behaves on heating like a mixture of calcium chromate and chromium trioxide. L. Schulerud could not prepare this salt. A. Naumann said that the dichromate is soluble in acetone. J. F. Bahr, A. Dalzell, and K. Preis and B. Rayman prepared **strontium dichromate,** $SrCr_2O_7.3H_2O$, from a soln. of strontium chromate in chromic acid. The crystals are coloured like those of potassium ferricyanide. G. N. Wyrouboff gave for the axial ratios of the monoclinic, prismatic crystals $a:b:c = 0{\cdot}6023 : 1 : 0{\cdot}5460$, and $\beta = 92° 32'$. The salt loses its water of crystallization at 110°; and at 220° all the water is expelled; and at a higher temp. oxygen is given off. K. Preis and B. Rayman, and W. Autenrieth obtained **barium dichromate,** $BaCr_2O_7$, by the action of a soln. of chromic acid on freshly precipitated barium chromate; and O. Mayer, by boiling barium chromate with chromic and nitric acids, and by adding barium chloride to a hot conc. soln. of chromic acid and washing the product with acetic acid. The brownish-yellow, or brownish-red, monoclinic prisms are decomposed by cold water into chromic acid and barium monochromate. O. Mayer said that the dichromate is not attacked by boiling acetic acid. According to J. F. Bahr, and E. Zettnow, the *dihydrate,* $BaCr_2O_7.2H_2O$, is formed by evaporating a soln. of barium chromate in chromic acid, but neither L. Schulerud nor W. Autenrieth could verify this. K. Preis and B. Rayman said that the dihydrate is produced by evaporating the mother-liquor from the preparation of the anhydrous salt. J. F. Bahr described the crystals as stellate groups of yellowish-brown needles; K. Preis and B. Rayman, as rhombic, brownish-yellow plates; and E. Zettnow, as dark yellow, doubly refracting scales which lose all their water at 120°. J. F. Bahr said that the salt is nearly all decomposed by water; and that barium dichromate separates from conc., aq. soln.; and barium monochromate from dil. aq. soln. For the equilibrium between barium chromate and dichromate, *vide* chromic acid.

B. Reinitzer[10] prepared **magnesium dichromate,** $MgCr_2O_7$; and he found the salt to be soluble in water; and slightly soluble in alcohol. G. A. Barbieri and F. Lanzoni obtained complex salts of magnesium dichromate with hexamethylenetetramine by the action of a conc. soln. of that base with potassium dichromate on a conc. soln. of magnesium acetate or sulphate. By evaporating in vacuo a soln. of a mol of zinc carbonate in 2 mols of cold chromic acid, J. Schulze[11] obtained dark reddish-brown crystals of **zinc dichromate,** $ZnCr_2O_7.3H_2O$. The crystals are hygroscopic in air; and freely soluble in water, but are decomposed by boiling water. The salt was also prepared by M. Gröger. C. O. Weber obtained what he regarded as *potassium zinc chromatodichromate,* $K_2Cr_2O_7.ZnCrO_4$. G. Krüss and O. Unger obtained a complex with mercuric cyanide; N. Parravano and A. Pasta, and S. H. C. Briggs, a complex with pyridine; and S. H. C. Briggs, a complex with aniline. J. Schulze obtained **cadmium dichromate,** $CdCr_2O_7.H_2O$, by the method employed for the zinc salt. The dark orange-brown crystals are easily soluble in water, and are not decomposed by that agent. G. Krüss and O. Unger, and M. Gröger also prepared this salt. N. Parravano and A. Pasta obtained complex salts with ethylenediamine, pyridine, and aniline. G. Krüss prepared hygroscopic **potassium cadmium dichromate,** $K_2Cr_2O_7.CdCr_2O_7.2H_2O$, which is soluble in water.

J. A. Atanasiu[12] found that in the electrometric titration of soln. of mercurous nitrate and potassium chromate the curve shows a break corresponding with

**mercurous dichromate,** $Hg_2Cr_2O_7$. A. J. Cox showed that **mercuric dichromate,** $HgCr_2O_7$, is also stable at 25°, with soln. having more than 10·46 mols of chromic acid per litre—Figs. 50 and 51—and this salt is the solid phase with soln. having between about 10·5 and 11·5 mols of chromic acid per litre. The same salt was prepared by A. Gawalowsky by the action of potassium dichromate on a soln. of mercuric nitrate. The deep carmine-red crystals were found by S. H. C. Briggs to form complex salts with pyridine. They also form complexes with other mercuric salts—chloride, cyanide, etc. K. A. Hofmann recommended a soln. of mercuric chromate in chromic acid for oxidizing carbon monoxide in gas-analysis. C. Hensgen prepared **ammonium oxydimercuriammonium dichromate,** $3(NH_4)_2Cr_2O_7[NH_2(HgOHg)]_2Cr_2O_7$, by boiling a soln. of ammonium dichromate with mercuric oxide; or by saturating a hot, conc. soln. of ammonium dichromate with yellow mercuric oxide, and washing with water, alcohol, and ether, the product which separates on cooling. The yellow needles or plates do not decompose in air. The salt decomposes with detonation when heated rapidly, and when slowly heated to 170°–200°, it forms a black, graphitic mass which detonates suddenly at a higher temp. It is insoluble in water, alcohol, and ether. Three-fourths of the nitrogen is evolved as ammonia when the salt is heated with potash-lye, and oxydimercuriammonium chromate is formed. The same product is obtained by treating the salt with aq. ammonia. The salt is freely soluble in hydrochloric acid, and sparingly soluble in dil. nitric or dil. sulphuric acid; and it is decomposed by warm, conc. acids.

G. Calcagni [13] prepared **aluminium oxydichromate,** $Al_2O(Cr_2O_7)_2$, as an amorphous paste by evaporating a soln. of precipitated aluminium hydroxide in chromic acid. R. E. Meyer obtained a soln. of **indium dichromate** by dissolving the oxide in a warm soln. of chromic acid; but on evaporation in a desiccator, he was unable to crystallize the resulting syrupy liquid. W. Crookes,[14] and M. Hebberling obtained **thallous dichromate,** $Tl_2Cr_2O_7$, by adding potassium dichromate to a soln. of a thallous salt. L. Schulerud emphasized the need for using an acidified soln. of the thallous salt, otherwise a mixture of thallous chromate and dichromate is precipitated. J. E. Willm obtained the dichromate by boiling the chromate with dil. sulphuric acid; and E. Carstanjen, by dissolving thallous carbonate in an excess of chromic acid. The orange-yellow or orange-red, crystalline powder is insoluble in water. F. J. Faktor found that thallous dichromate is somewhat soluble in water; and with a soln. of sodium thiosulphate, it forms yellow chromate, $Tl_2CrO_4$. If the soln. of the dichromate in sodium sulphate is warmed with ammonium chloride, hydrated chromic oxide is precipitated.

O. Mayer [15] obtained **lead dichromate,** $PbCr_2O_7$, by treating a soln. of lead acetate with chromic acid in the presence of conc. nitric acid, sp. gr. 1·4; K. Preis and B. Rayman, by treating lead chromate with a conc. soln. of chromic acid—cold or hot; and E. Hatschek, by the action of ammonium chromate on a soln. of lead nitrate. E. Hatschek also studied the formation of the dichromate by allowing the ammonium dichromate to diffuse into an agar-agar soln. of lead nitrate; and V. Moravek, by the diffusion of lead nitrate into gels. of potassium dichromate. A. J. Cox studied the conditions of its formation from lead oxide and chromic acid—*vide* Fig. 55. It is formed when a mol of lead oxide is shaken with a sat. soln. of 2·5 mols of chromic acid at 25°. The excess of chromic acid is washed out with a more dil. soln. of chromic acid, and the product dried by press. between porous tiles, and then in a desiccator over calcium chloride. K. Elbs and R. Nübling prepared the dichromate by electrolyzing a 130 per cent. soln. of chromic acid between lead electrodes with an anode density of 4 to 3 amps. per sq. dm. at 15°–20°. They also obtained evidence of the formation of *plumbic dichromate,* $Pb(Cr_2O_7)_2$. The preparation of lead dichromate was also studied by J. Milbauer, who found that the dichromate is precipitated from soln. which are seven times molar with respect to $CrO_3$. The crystals cannot be washed by water without hydrolysis, but they can be freed from chromic acid by washing with a

10 per cent. soln. of glacial acetic acid in acetone. Electrolytic processes were studied by W. Borchers, and C. Lückow. K. Preis and B. Rayman obtained a *dihydrate*, $PbCr_2O_7.2H_2O$, but this has not been confirmed. Lead dichromate appears as a reddish-brown powder, or in brick-red needles, or as a crystalline powder. It is decomposed by water into lead chromate and chromic acid; it is stable in a soln. with at least 6·87 mols of $CrO_3$ per litre at 25°. It is soluble in soda-lye.

As indicated in connection with the basic bismuth chromates, there is a possibility that *bismuth hydroxychromate*, $Bi(OH)(CrO_4)$, is **bismuthyl dichromate**, $(BiO)_2Cr_2O_7.H_2O$; and that *bismuthyl quaterchromate*, $Bi_2O_3.4CrO_3.H_2O$, is **bismuthyl hydroxydichromate**, $Bi(OH)(Cr_2O_7)$. A. J. Cox[16] did not find bismuth dichromate on the equilibrium diagram, Fig. 63. K. Preis and B. Rayman prepared **potassium bismuthyl dichromate**, $K_2Cr_2O_7.(BiO)_2Cr_2O_7$, by mixing soln. of 2 mols of bismuth nitrate, and 3 mols of potassium chromate, and allowing the precipitate to stand in contact with the mother-liquor to crystallize. The pale or dark orange-red, granular or scaly powder is decomposed by water. It is soluble in hydrochloric acid. If this salt be warmed with an excess of a conc. soln. of chromic acid, it forms a dark red, crystalline mass of **potassium bismuth hydroxydichromate**, $K_2Cr_2O_7.2Bi(OH)(Cr_2O_7)H_2O$. It is decomposed by water.

G. Calcagni[17] prepared a hygroscopic, amorphous paste of **chromium dichromate**, $Cr_2(Cr_2O_7)_3$, by evaporating a soln. of chromic oxide in chromic acid. P. Pfeiffer prepared **chromic trisethylenediaminodichromate**, $[Cr\ en_3]_2(Cr_2O_7)_3.2H_2O$, by the action of potassium dichromate on a soln. of the chloride. The yellow needles are slightly soluble in cold water. The salt is decomposed by heat or by exposure to sunlight. O. T. Christensen obtained **chromic nitritopentamminodichromate**, $[Cr(NH_3)_5NO_2]Cr_2O_7$, analogous to the chromate (*q.v.*). A. Werner and J. von Halban made **chromic thiocyanatopentamminodichromate**, $[Cr(NH_3)_5SCy]Cr_2O_7$, in an analogous manner. E. Wilke-Dörfurt and H. G. Mureck prepared **chromic hexantipyrinodichromate**, $[Cr(C_{10}H_{12}N_2)_6](Cr_2O_7)_3$. W. J. Sell, and E. Wilke-Dörfurt and K. Niederer prepared **chromic hexacarbamidodichromate**, $[Cr(CON_2H_4)_6]_2(Cr_2O_7)_3.3H_2O$, as well as **chromic hexacarbamidoperchloratodichromate**, $[Cr(CON_2H_4)_6](Cr_2O_7)ClO_4$; **chromic hexacarbamidodisulphatodichromate**, $[Cr(CON_2H_4)_6]_2(Cr_2O_7)(SO_4)_2.5H_2O$; **chromic hexacarbamidonitratodichromate**, $[Cr(CON_2H_4)_6](NO_3)(Cr_2O_7).H_2O$; **chromic chlorodichromate**, $[Cr(CON_2H_4)_6](Cr_2O_7)Cl.2H_2O$; and **chromic hexacarbamidobromodichromate**, $[Cr(ON_2H_4)_6](Cr_2O_7)Br.H_2O$. They also made **chromic hexacarbamidotetraborofluodichromate**, $[Cr(CON_2H_4)_6]_2(Cr_2O_7)(BF_4)_4$, but not $[Cr(CON_2H_4)_4](Cr_2O_7)BF_4$. G. Calcagni prepared **molybdenum dichromate**, $Mo(Cr_2O_7)_3$, as in the case of the chromium salt; but neither **tungsten dichromate**, nor **uranium dichromate** could be so prepared.

According to M. Gröger,[18] **manganese dichromate**, $MnCr_2O_7$, has not been prepared, but N. Parravano and A. Pasta obtained a complex salt with aniline; and with pyridine. S. H. C. Briggs also prepared a complex with pyridine. According to S. Husain and J. R. Partington, chromic acid acting on an excess of solid manganese carbonate yields a dark red soln. probably containing manganese dichromate. Only partly decomposed solid products could be obtained from this soln. Attempts to prepare double manganese dichromate and potassium chromate were not successful, because the latter is converted into dichromate with the precipitation of manganese dioxide. G. Calcagni prepared **ferric oxybisdichromate**, $Fe_2O(Cr_2O_7)_2$, or $(FeCr_2O_7)_2O$, from a soln. of ferric hydroxide in chromic acid. According to S. Husain and J. R. Partington, the prolonged action of a soln. of chromic acid on an excess of precipitated ferric hydroxide at 80° to 90°, yielded a soln., which, on evaporation at 90°, gave a residue with the composition of **ferric dichromate**, $Fe_2(Cr_2O_7)_3$, after it had been dried in vacuo. Ferric dichromate is a hygroscopic, brown solid which hydrolyzes when the aq. soln. is largely diluted. It decomposes a little at 100°, and at 140° the chromate radicle is decomposed,

forming a black residue which slowly dissolves in boiling, conc. hydrochloric acid, forming a green soln. E. Wilke-Dörfurt and H. G. Mureck prepared ferric hexantipyrinodichromate, $[Fe(C_{10}H_{12}N_2)_6](Cr_2O_7)_3$.

J. Schulze [19] obtained a soln. of **cobalt dichromate,** by dissolving cobaltous oxide in a soln. of chromic acid. The liquid contained $CoO : CrO_3$ in the molar ratio 1 : 2. G. Krüss and O. Unger obtained **ammonium cobaltous dichromate,** $(NH_4)_2Cr_2O_7.CoCr_2O_7.2H_2O$, by evaporating in vacuo a hot conc. soln. of equimolar parts of ammonium dichromate and cobalt nitrate. The black, tabular crystals lose their water of crystallization at 105°. O. W. Gibbs prepared **cobaltic hexamminodichromate,** $[Co(NH_3)_6]_2(Cr_2O_7)_3.nH_2O$, in orange needles, by adding ammonium dichromate to a conc. soln. of the nitrate of the base. A. Werner and K. Dawe prepared **cobaltic bispropyldiamminodiamminodichromate,** $[Copn_2(NH_3)_2]_2(Cr_2O_7)_3.2H_2O$; and O. W. Gibbs, **cobaltic aquopentamminodichromate,** $[Co(NH_3)_5(H_2O)]_2(Cr_2O_7)_3.3H_2O$, by adding potassium dichromate to an aq. soln. of the nitrate. O. W. Gibbs also obtained **cobaltic nitritopentamminodichromate,** $[Co(NH_3)_5NO_2]Cr_2O_7$, by adding potassium dichromate to the corresponding nitrate; the orange-yellow, crystalline precipitate may be crystallized from water acidified with acetic acid. S. M. Jörgensen obtained **cobaltic cisdinitritotetramminodichromate,** $[Co(NH_3)_4(NO_2)_2]_2Cr_2O_7$, as in the case of the corresponding monochromate; so also with **cobaltic transdinitritotetramminodichromate,** prepared by O. W. Gibbs; with **cobaltic nitratopentamminodichromate,** $[Co(NH_3)_5NO_3]Cr_2O_7.H_2O$, prepared by S. M. Jörgensen, and O. W. Gibbs; with **cobaltic chloropentamminodichromate,** $[Co(NH_3)_5Cl]_2Cr_2O_7$, obtained by S. M. Jörgensen; with **cobaltic iodopentamminodichromate,** $[Co(NH_3)_5I]_2Cr_2O_7$, prepared by A. Werner; with **cobaltic dichlorotetramminodichromate,** $[Co(NH_3)_4Cl_2]_2Cr_2O_7$, prepared by A. Werner and A. R. Klein—G. Vortmann regarded the salt as *monohydrated;* and with A. Werner and A. A. Wolberg's **cobaltic dibromotetramminodichromate,** $[Co(NH_3)_4Br_2]_2Cr_2O_7$. G. Vortmann prepared **cobaltic dioxydecamminodichromate,** $[CoO_2(NH_3)_{10}]_2(Cr_2O_7)_5.8H_2O$, from soln. of the chloride and potassium dichromate. P. Ray and P. V. Sarkar obtained **cobaltic chromatotetramminodichromate,** $[Co(NH_3)_4(CrO_4)]_2Cr_2O_7.H_2O$, by the action of chromic acid on the carbonatotetramminonitrate—it loses its water over sulphuric acid; S. H. C. Briggs obtained the dihydrate by the action of potassium dichromate on a soln. of diaquotetramminonitrate. P. Ray and P. V. Sarkar found that **cobaltic dichromatotetramminodichromate,** $[Co(NH_3)_4(Cr_2O_7)]_2Cr_2O_7.H_2O$, is formed if a larger proportion of chromic acid be employed. P. Ray and P. V. Sarkar also prepared **cobaltic dichromatopentamminochromate,** $[Co(NH_3)_5(Cr_2O_7)]_2CrO_4.3H_2O$; from the corresponding carbonato-salts. S. H. C. Briggs prepared **cobaltic chromatoaquotriamminodichromate,** $[Co(NH_3)_3(H_2O)CrO_4]_2Cr_2O_7.2H_2O$, from soln. of cobalt trinitratotriammine and of sodium dichromate. P. Ray and P. V. Sarkar found that when cobaltic chromatopentamminochromate is recrystallized from dil. acetic acid, it furnishes **cobaltic aquopentamminochromatobisdichromate,** $[Co(NH_3)_5(H_2O)]_2(CrO_4)(Cr_2O_7)_2.H_2O$. S. H. C. Briggs added a cobaltic diaquotetrammino-salt to a large excess of sodium dichromate and obtained brownish-black crystals of **cobaltic enneamminodichromate,** $Co_2(Cr_2O_7)_3.9NH_3.4H_2O$.

S. H. C. Briggs [20] prepared **nickel dichromate,** $NiCr_2O_7.1\frac{1}{2}H_2O$, by boiling on an oil-bath 5·5 grms. of nickel carbonate (with 70 per cent. NiO), with a soln. of 10·5 grms. of chromium trioxide in 7·5 c.c. of water in a flask fitted with a reflux condenser. The crystalline powder has the colour of silver chromate. It deliquesces in air; and is slowly dissolved by cold water, but rapidly by hot water. G. Chiavarino studied the ethylendiamine salt $NiCr_2O_7.3C_2H_4(NH_2)_2$.

G. B. Buckton [21] prepared **platinous tetramminodichromate,** $Pt[(NH_3)_4]Cr_2O_7$, by treating a soln. of the chloride with chromic acid, and the product drying in vacuo. When crystallized from hot soln. it resembles lead monochromate. It gives off water, ammonia, and nitrogen when heated, leaving platinum, and chromic oxide

as a residue. It is sparingly soluble in water ; insoluble in alcohol ; and when boiled with alcohol and hydrochloric acid it forms aldehyde, chromic chloride, and platinic dichlorotetramminochloride. S. G. Hedin obtained **platinic sulphatotetrapyridinodichromate,** $[Pt(C_5H_5N)_4(SO_4)]Cr_2O_7$, by the method used for the corresponding chromate (*q.v.*). O. Carlgren and P. T. Cleve prepared **platinic dinitritotetramminodichromate,** $[Pt(NH_3)_4(NO_2)_2]Cr_2O_7$, by the action of hydrogen dioxide on the precipitate obtained by mixing soln. of platinous tetramminochloride and potassium dichromate. The lemon-yellow powder detonates when heated. P. T. Cleve prepared **platinic dinitratotetramminodichromate,** $[Pt(NH_3)_4(NO_3)_2]Cr_2O_7$ by the method used for the corresponding chromate ; and likewise with **platinic dichlorotetramminodichromate,** $[Pt(NH_3)_4Cl_2]Cr_2O_7$. He also obtained **platinic hydroxyacetatotetramminodichromate,** $[Pt(NH_3)_4(HO)(CH_3COO)]Cr_2O_7.H_2O$, in orange-yellow, six-sided plates from the corresponding chloride and potassium dichromate. He also made **platinic hydroxysulphatotetramminodichromate,** $[Pt(NH_3)_4(OH)(SO_4)]_2Cr_2O_7$, in a similar way ; likewise also with **platinic hydroxychlorotetramminodichromate,** $[Pt(NH_3)_4(OH)Cl]Cr_2O_7$. P. T. Cleve obtained **platinic dihydroxydiamidohexamminodichromate,**

$$\left[\begin{matrix} HO \\ (NH_3)_3 \end{matrix}\!\!\searrow Pt \lessdot \begin{matrix} NH_2 \\ NH_2 \end{matrix} \gtrdot Pt \swarrow\!\!\begin{matrix} OH \\ (NH_3)_3 \end{matrix}\right](Cr_2O_7)_2,$$

as an orange-red precipitate from the corresponding nitrate and potassium dichromate.

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## § 17. The Trichromates

M. Siewert [1] evaporated a soln. of ammonium dichromate in nitric acid, and obtained **ammonium trichromate,** $(NH_4)_2Cr_3O_{10}$. E. Jäger and G. Krüss recommended nitric acid of sp. gr. 1·39; but added that it is more convenient to prepare the salt from a soln. of ammonium dichromate in a conc. soln. of chromic acid. F. A. H. Schreinemakers studied the conditions of equilibrium, and his results are summarized in Fig. 29. The dark garnet-red, rhombic bipyramids were found by G. N. Wyrouboff to have the axial ratios $a:b:c=0{\cdot}8446:1:0{\cdot}8344$; the (100)-cleavage is distinct. The optic axial angle $2E=44°\ 30'$; and the optical character is positive. E. Jäger and G. Krüss gave 2·329 at 10°, and 2·342 at 13° for the sp. gr. M. Siewert said that the salt darkens at 110°–120°, and E. Jäger

and G. Krüss said that the darkening which appears at 160°–170° is a sign of decomposition which begins at about 150°. Detonation occurs at about 190°. The residue is chromic oxide, or, according to M. Siewert, chromic oxide mixed with chromium trioxide. Water, nitrogen and nitrogen oxides—*e.g.* $NO_2$—are evolved. W. C. Ball said that the thermal decomposition resembles that with the dichromate (*q.v.*). The salt does not deliquesce, but it slowly decomposes in moist air forming chromic acid and ammonium dichromate; similarly also in contact with water.

F. A. H. Schreinemakers [2] did not find **lithium trichromate,** $Li_2Cr_3O_{10}$ in his study of the ternary system $Li_2O$–$CrO_3$–$H_2O$ at 30°—Fig. 31. A. Stanley prepared dark red deliquescent crystals of **sodium trichromate,** $Na_2Cr_3O_{10}.H_2O$, by evaporating over sulphuric acid a soln. of sodium dichromate in chromic acid. The conditions of equilibrium, worked out by F. A. H. Schreinemakers, are summarized in Fig. 32. The crystals effloresce over sulphuric acid. The deliquescent crystals are soluble in water without decomposition even at 100°; and F. A. H. Schreinemakers found that at 30° a sat. soln. contains 70 per cent. $Na_2Cr_3O_{10}$. F. Mylius and R. Funk found that a soln. sat. at 18° contains 80·60 per cent. of salt and has a sp. gr. 2·059; and they gave for the percentage solubility at 0°, 15°, 55°, and 99°, respectively 80·03, 80·44, 82·68, and 85·78.

E. Mitscherlich [3] prepared **potassium trichromate,** $K_2Cr_3O_{10}$, from a soln. of potassium dichromate and nitric acid; F. Bothe recommended working with nitric acid of sp. gr. 1·210, and at 60°; E. Jäger and G. Krüss used nitric acid of sp. gr. 1·19. C. Schmidt used conc. nitric acid, but G. N. Wyrouboff said that if the nitric acid be too conc.—over 1·41 sp. gr.—some tetrachromate is formed. H. Reinsch, and C. J. B. Karsten observed the tendency of potassium nitrate to crystallize out with the trichromate in nitric acid soln.; and L. Darmstädter mistook the impure product for nitrochromate. M. Siewert separated the product from potassium nitrate by fractional crystallization. C. von Hauer, M. Siewert, and E. Jäger and G. Krüss obtained the trichromate by evaporating over sulphuric acid a soln. of potassium dichromate in chromic acid; F. A. H. Schreinemakers, and I. Koppel and E. Blumenthal studied the conditions of equilibrium, and the results are summarized in Figs. 36 to 41. Potassium trichromate furnishes deep red, prismatic crystals; and F. Bothe reported that the monoclinic prisms have the axial ratios $a:b:c=0{\cdot}8437:1:0{\cdot}8318$, and $\beta=101°\,0'$; the (010)-cleavage is distinct. F. Bothe gave 3·613 for the sp. gr.; H. G. F. Schröder, 2·676–2·702; L. Playfair and J. P. Joule, 2·655; and E. Jäger and G. Krüss, 2·667 at 10°—crystallized from chromic acid—and 2·648 at 11°—crystallized from nitric acid. The hardness is 2·5. I. Traube found the drop-weight of the molten trichromate to be 231 mgrms. F. Bothe said that the salt decrepitates a little when heated, and melts at 145°–150°; E. Jäger and G. Krüss said that the trichromate blackens at 220°, and melts at 250°. E. Groschuff said that the salt decomposes when melting. M. Berthelot gave for the heat of formation in the solid state: $(K_2CrO_4,2CrO_3)$ =14·1 Cals.; and T. Graham gave for the heat of soln., −14·2 Cals. On exposure to air, the crystals lose their lustre and become opaque. The salt is freely soluble in water and there is a small fall in temp., and the trichromate decomposes into dichromate and chromic acid. P. Walden also inferred from the electrical conductivity, $\mu$ mho of the aq. soln. of a mol of the salt in $v$ litres of water at 25°, *viz.*

| $v$ | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|
| $\mu$ | 275·9 | 282·9 | 286·1 | 286·4 | 283·4 | 278·2 |

that the salt is partially decomposed. L. A. Welo studied the magnetic susceptibility. F. Bothe found that the trichromate is soluble in alcohol, and the alcoholic soln. rapidly decomposes in light. A. Naumann found that the salt is soluble in acetone. G. N. Wyrouboff studied solid soln. of potassium and ammonium trichromates, and saw that the hexagonal crystals have the axial ratio $a:c=1:1{\cdot}0844$ with 58·5 to 69·7 per cent. of the ammonium salt.

F. A. H. Schreinemakers and H. Filippo [4] showed the conditions of equilibrium,

Fig. 46, for **rubidium trichromate,** $Rb_2Cr_3O_{10}$, in soln. of chromic acid; and F. A. H. Schreinemakers and D. J. Meijeringh, the conditions of equilibrium, Fig. 47, of **cæsium trichromate,** $Cs_2Cr_3O_{10}$. The dark red, trigonal crystals were stated by F. R. Fraprie to have the axial ratio $a:c=1:1{\cdot}5549$ and not to be isomorphous with the other trichromates.

M. Gröger [5] could not prepare **copper trichromate,** $CuCr_3O_{10}$. H. von Foullon passed carbon dioxide into a soln. of calcium chromate and obtained a precipitate corresponding with **calcium oxytrichromate,** $CaO.CaCr_3O_{10}$. K. Preis and B. Rayman prepared garnet-red deliquescent crystals of **strontium trichromate,** $SrCr_3O_{10}.3H_2O$, by the method employed in preparing the dichromate, but using a large excess of chromic acid. J. F. Bahr prepared **potassium barium trichromate,** $K_2Cr_3O_{10}.2BaCr_3O_{10}.3H_2O$, from a chromic acid soln. of barium and potassium dichromates. The reddish-brown needles are very deliquescent, and are decomposed by water.

M. Gröger [6] prepared dark red, deliquescent crystals of **zinc trichromate,** $ZnCr_3O_{10}.3H_2O$, by evaporating in vacuo a soln. of zinc dichromate in chromic acid. He also obtained **cadmium trichromate,** $CdCr_3O_{10}.H_2O$, in dark reddish-brown crystals by an analogous process. A. Gawalowsky obtained pale red crystals of *mercuric polychromate* by the action of an acidified soln. of potassium dichromate on mercury.

W. Crookes [7] obtained **thallous trichromate,** $Tl_2Cr_3O_{10}$, by digesting the chromate with sulphuric acid; and J. E. Willm, by digesting the dichromate with nitric acid. The red, crystalline powder behaves like the monochromate towards aq. and alcoholic hydrochloric acid. 100 grms. of water at 15° dissolve 0·0355 grm. of the trichromate, and at 100°, 0·2283 grm.


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## § 18. The Tetrachromates

G. N. Wyrouboff [1] reported **ammonium tetrachromate,** $(NH_4)_2Cr_4O_{13}$, to be formed by crystallization from a soln. of ammonium dichromate in hot nitric acid of sp. gr. 1·41. E. Jäger and G. Krüss could not obtain the salt in this way, but

they obtained it by slowly cooling a soln. of the trichromate in nitric acid of sp. gr. 1·39. F. A. H. Schreinemakers studied the conditions of equilibrium, and the results are summarized in Fig. 29. The brownish-red, crystalline aggregates are less stable than the lower chromates. E. Jäger and G. Krüss observed that the salt is hygroscopic, and is decomposed by moisture into the dichromate and chromic acid. The crystalline salt is stable in a dry atmosphere. It blackens when heated to 160°, melts at 170°, and decomposes suddenly at 175°, giving off nitric oxide, etc., and leaving a mixture of chromic oxide and chromium trioxide. J. J. Pohl reported crystals of *ammonium tetrachromate*, thought to be $(NH_4)_{10}Cr_4O_{17}$, in the preparation of the normal tetrachromate. J. Schabus found the monoclinic crystals had the axial ratios $a : b : c = 0{\cdot}7458 : 1 : 0{\cdot}4955$, and $\beta = 106° 51'$.

F. A. H. Schreinemakers could not prepare **lithium tetrachromate,** $Li_2Cr_4O_{13}$; but he showed that **sodium tetrachromate,** $Na_2Cr_4O_{13}.H_2O$, can exist under the conditions indicated in Fig. 34. F. Mylius and R. Funk prepared this salt by evaporating a soln. of sodium chromate in an excess of chromic acid. The garnet-red, deliquescent plates melt at 40°–50° with the separation of chromium trioxide. The salt dissolves in water without decomposition. A sat. soln. at 18° has 74·60 per cent. of $Na_2Cr_4O_{13}$, and has a sp. gr. of 1·926; and at 0°, 16°, and 22°, the respective percentage solubilities are 72·19, 74·19, and 76·01.

M. Siewert prepared potassium tetrachromate, $K_2Cr_4O_{13}$, by evaporating a soln. of potassium trichromate in conc. nitric acid slowly on a sand-bath, and cooling the mixture. The crystalline plates have the colour of mercuric iodide, and are freed from nitric acid by press. on porous titles, and by drying at 140°. E. Jäger and G. Krüss, and G. N. Wyrouboff used nitric acid of sp. gr. 1·4; and C. Schmidt, acid of sp. gr. 1·48–1·52. The contamination of the salt with nitrate led L. Darmstädter to regard it as a nitrochromate. E. Jäger and G. Krüss, and G. N. Wyrouboff obtained it by crystallization from a soln. of the trichromate in aq. chromic acid. F. A. H. Schreinemakers, and I. Koppel and E. Blumenthal studied the conditions of equilibrium, and the results are summarized in Figs. 36 to 41. H. Schwarz found that a soln. of a mol of potassium dichromate and 2 mols of sulphuric acid, first deposits crystals of the dichromate, and afterwards a mixture of potassium tetrachromate and sulphate. Potassium tetrachromate forms brownish-red or carmine-red, 8-sided plates and prisms, which are monoclinic; G. N. Wyrouboff gave for the axial ratios $a : b : c = 0{\cdot}797 : 1 : 1{\cdot}110$, and $\beta = 91° 42'$. The deliquescent crystals are stable in air; and E. Jäger and G. Krüss said that their sp. gr. is 2·649 at 11°; and that they melt at 215°; they are decomposed by water into trichromate and chromic acid.

F. Mylius and J. von Wrochem obtained dark red crystals of **calcium tetrachromate,** $CaCr_4O_{13}.6H_2O$, by evaporating over sulphuric acid a soln. of calcium carbonate in an excess of chromic acid. The salt is soluble in water.

C. F. Rammelsberg found that a soln. of chromic acid free from sulphuric acid, and half saturated with ammonia furnished a brownish-yellow salt—thought to be *ammonium hexachromate*. It decomposed with incandescence when heated. E. Jäger and G. Krüss could obtain only the dichromate by this process; and they were unable to isolate a more complex salt than the tetrachromate. This agrees with F. A. H. Schreinemaker's observations—Fig. 29.


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## § 19. Perchromic Acid and the Perchromates

In 1847, L. C. A. Barreswil,[1] in his memoir: *Sur un nouveau composé oxygèné du chrome*, described how a deep blue soln. is produced when a conc. soln. of chromic acid is mixed with hydrogen dioxide. The soln. immediately begins to decompose with the evolution of oxygen, and this decomposition occurs more quickly with conc. soln. and with vigorous agitation. If sulphuric acid be mixed with potassium dichromate, and treated with hydrogen dioxide, oxygen is evolved and a soln. of chromic sulphate is formed. If ether be shaken up with the blue soln., the aq. layer is decolorized, and the ethereal liquor retains the blue product. The ethereal soln. is more stable than the aq. soln. If the ethereal soln. be evaporated, a conc. is attained at which the liquor suddenly decomposes with the evolution of oxygen and the formation of chromic acid. It is assumed that the blue soln. contained a perchromic acid $CrO_{3+n}$ formed in accord with $2CrO_3+2nH_2O_2 \rightarrow 2CrO_{3+n}+2nH_2O$; and that the decomposition progresses $2CrO_{3+n} \rightarrow Cr_2O_3+(2n+3)O$, or $CrO_{3+n} \rightarrow CrO_3+nO$. F. H. Storer said that the blue coloration is so sensitive that it enables one part of potassium dichromate to be detected in 30,000 to 40,000 parts of water. G. Werther said that the presence of 0·0001 part of vanadate will mask the effect with 0·0001 part of chromate; and C. Reichard noted that the disturbing effect of the molybdate and tungstate is not so great as that of the vanadate. C. Reichard observed that the presence of sodium hydrophosphate or hydroarsenate removes the injurious effect of vanadium.

W. M. Grosvenor found that the blue compound is also soluble in ethyl acetate or valerate, amyl chloride, amyl alcohol, and in amyl formate, acetate, butyrate, or valerate. The blue substance is not dissolved by carbon disulphide, benzene, light petroleum, toluene, nitrobenzene, aniline, paraffin and turpentine, carbon tetrachloride, chloroform, castor oil, bergamot oil, and oil of wintergreen. The soln. in ethyl acetate is said to be the most stable, but even that decomposes in about 23 hrs. G. Griggi said that the soln. in amyl alcohol is more stable than in ordinary ether, but W. M. Grosvenor did not agree. According to L. C. A. Barreswil, alkaloids—quinine, strychnine, etc.—in ethereal soln. form dirty violet precipitates insoluble in ether; and when the precipitate is dried and treated with an acid, and ether, the blue soln. is again formed.

H. Aschoff found that the blue soln. is decolorized by ferrous salts; and, according to W. P. Jorissen and L. T. Reicher, by oxalic acid. With an excess of alkali-lye, L. C. A. Barreswil observed that oxygen is evolved and alkali chromate is formed. H. Aschoff found that lead oxide behaves like the alkali. C. F. Schönbein made some observations on the action of alkali on the blue soln. H. Aschoff found that if a dil. soln. of potassium hydroxide be added to the soln. until the ethereal layer is pale blue, water now colours the neutral aq. layer brownish-violet. The addition of more alkali results in the evolution of oxygen, and the formation of yellow alkali chromate. It is therefore inferred that the soln. of the free perchromic acid is blue, and that the salts are violet. In general, as shown by M. Martinon, acids decomposed the blue substance into salts of chromic oxide and oxygen, while alkalies form chromates.

M. Berthelot showed that with strong acids and a soln. of dichromate, hydrogen dioxide gives the blue colour of the hypothetical perchromic acid; with the weaker acetic or phosphoric acid, the colour is violet not blue—due, it is suggested, to the formation of a brown substance along with the perchromic acid; and with still weaker boric or hydrocyanic acid, the colour is brown and the rate of decomposition is slow. With a moderately conc. soln. of chromic acid, the liquid is first blue, then violet, brown, or even green; but with dil. soln., at 10°, only traces of the blue perchromic acid are formed. The brown substance is the chief product. The action is most regular with an aq. soln. of a mol. of potassium dichromate per 16 litres, and an eq. quantity of a soln. containing a mol of hydrogen dioxide per 2 litres. The liquid first darkens in colour, rapidly becoming deep brown, and

oxygen is liberated with effervescence, and during the reaction the liquid contains only traces of perchromic acid. The liquid then becomes clear and acquires its original colour—it contains neither hydrogen dioxide nor reduced chromic oxide. The same quantity of potassium dichromate will decompose an unlimited quantity of hydrogen dioxide. The brown intermediate product is probably a compound of hydrogen peroxide with chromic oxide: it decomposes rapidly, with regeneration of chromic acid, liberation of oxygen, and formation of water. As the thermal measurements show, the heat liberated by the reaction is identical with that liberated by the decomposition of hydrogen peroxide.

The brown colour of the unstable intermediate product points to the formation of chromium chromate. The hydrogen dioxide oxidizes the chromium chromate forming chromic acid and water. All this characterizes a catalytic reaction. Attempts by E. H. Riesenfeld, and E. Spitalsky to work out a detailed explanation of the catalyzed reaction have not been successful. When a large excess of hydrogen dioxide is present, the rate of decomposition is approximately proportional to the conc. of the chromic acid. If $C_1$ denotes the conc. in mols of $K_2CrO_4$ per litre, and $k_1$ the velocity constant,

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $C_1$ . . | 0·001674 | 0·003132 | 0·02205 | 0·0313 | 0·05105 | 0·0674 | 0·1020 |
| $k_1$ (obs.) . | 0 | 6·7 | 14·4 | 15·9 | 23·5 | 29·4 | 46·0 |
| $k_1$ (calc.) . | 0·8 | 1·4 | 10·1 | 14·4 | 23·5 | 31·0 | 46·8 |

The reaction with dichromate is faster than with monochromate; and if $C_2$ denotes the conc. in mols of $K_2Cr_2O_7$ per litre, and $k_2$, the velocity constant of a first order reaction,

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $C_2 \times 10^4$ . . | 0·3 | 1·2 | 2·4 | 4·8 | 7·83 | 9·6 | 45·4 | 90·8 |
| $k_2$ (obs.) . . | 4·5 | 17·2 | 33·7 | 65·3 | 100 | 123 | 394 | 829 |
| $k_2$ (calc.) . . | 4·1 | 16·4 | 32·0 | 65·8 | 108 | 123 | 394 | 829 |

The calculated values from $C_2 = 9{\cdot}6 \times 10^{-4}$ are no longer in accord with the observed. With dichromate alone, or in feebly acidic soln., some of the dichromate is reduced to a tervalent chromic salt; the proportion reduced depends on the acidity, *i.e.* on the $H^{\cdot}$-ion conc.; thus, with soln. containing 0·00546 mol Cr per litre at 25°, the percentage proportions of tervalent chromium are:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $[H^{\cdot}]$ | 0 | 0·00182 | 0·00354 | 0·00547 | 0·00783 | 0·00818 | 0·01089 |
| $Cr^{\cdots}$. | 2·0 | 8·7 | 18·9 | 28·5 | 36·2 | 43·6 | 57·5 per cent. |

These are equilibrium values in the sense that if a mixture contains more than this proportion of $Cr^{\cdots}$, oxidation to chromate occurs. E. Spitalsky found that when hydrogen dioxide is present in considerable excess, the rate at which it is decomposed is nearly independent of its conc., being approximately proportional to the cube root of the dioxide conc., but when the dioxide conc. has diminished to such an extent that the ratio $H_2O_2 : CrO_3$ is not more than 10 : 1, the velocity suddenly rises to two or three times its former value and then falls rapidly to zero, the dioxide being completely decomposed. The decomposition is relatively less rapid the greater the initial dioxide conc. for a definite conc. of chromic acid. When the dioxide is present in considerable excess, the rate of decomposition is approximately proportional to the chromic acid conc. The reaction velocity at any instant is completely determined by the dioxide and chromic acid conc. at that instant—for example, the sharp maximum in the velocity curve occurs at the same dioxide conc. for a definite chromic acid conc., independent of the initial conc. of the dioxide. E. H. Riesenfeld inferred that the $H_3CrO_8$-acid is first formed by the consumption of $H^{\cdot}$-ions; and as the acidity of the soln. is reduced, $H_3CrO_7$-acid appears. This is in harmony with E. Spitalsky's observation that a definite proportion of the chromic acid catalyst is reduced to a tervalent chromium salt. E. I. Orloff also discussed these complex reactions; and G. N. Ridley reviewed the general properties of perchromic acid.

H. Moissan said that the blue compound cannot be formed by the action of ozone, on a soln. of chromic acid, although A. Mailfert said that perchromic acid is formed if ether be also present. H. Moissan added that the blue perchromic acid is produced by the electrolysis of soln. of chromic acid only when hydrogen dioxide is first formed. E. H. Riesenfeld found that when a soln. of 16·6 grms. of chromic acid in 100 c.c. of a 30-per cent. soln. of sulphuric acid is electrolyzed, using platinum electrodes, and a porous cathode cell cooled by means of ether and carbon dioxide, a higher oxidation product of chromium, which can be detected by precipitation with ammonia, is probably formed, but decomposes as the conc. increases until the velocity of formation becomes equal to that of decomposition. Since chromic oxide, $Cr_2O_3$, and not chromic acid, is formed by the decomposition, the quantity of oxygen lost is greater than that produced by the electrolysis.

Two methods have been employed for finding the nature of the blue product: (i) By isolating the substance, its salts or their equivalent; and (ii) By determining the oxidizing power or the amount of oxygen set free during its decomposition. L. C. A. Barreswil found that when an acidified soln. of potassium dichromate is treated with hydrogen dioxide, 4 mols of oxygen are given off per mol of $K_2Cr_2O_7$; and he assumed that the perchromic acid, $Cr_2O_7.H_2O$, is formed as an intermediate compound. H. Aschoff represented the reaction: $2CrO_3+H_2O_2=H_2O+Cr_2O_7$ followed by $Cr_2O_7+4H_2O_2\rightarrow Cr_2O_3+4H_2O+4O_2$. B. C. Brodie found that with an excess of chromic acid, 6 gram-atoms of oxygen are evolved per 2 mols of $CrO_3$; and with an excess of hydrogen dioxide, 9 gram-atoms of oxygen; while T. Fairley's observations led him to assume that the intermediate perchromic acid is $CrO_6.3H_2O$. M. Martinon found that the maximum depth of blue coloration is developed when 2 mols. of $CrO_3$ and 4 mols. of $H_2O_2$ are present, and hence he regarded the perchromic acid as $4H_2O_2.2CrO_3$, *i.e.* $H_4CrO_7$, with the anhydride $CrO_5$. A. Carnot found that chromic acid is quantitatively reduced by hydrogen dioxide, and M. Berthelot observed that the amount of oxygen developed depends on whether the hydrogen dioxide is poured into the chromic acid or conversely. In the first case the result agrees with: $2CrO_3+3H_2O_2+3H_2SO_4=Cr_2(SO_4)_3+3O_2+6H_2O$, *i.e.* the chromic acid and hydrogen dioxide each lose the same quantity of oxygen. In the second case, the reaction seems to occur in two stages, $2CrO_3+H_2O_2=Cr_2O_7+H_2O$, and then $Cr_2O_7+4H_2O_2=Cr_2O_3+4H_2O+4O_2$ when 1·66 times as much oxygen is derived from the hydrogen dioxide as from the chromium trioxide. The intermediate $Cr_2O_7$ is considered to be the anhydride of the blue perchromic acid. E. Baumann confirmed M. Berthelot's conclusions; and observations were also made by A. Bach, and L. Marchlewsky. E. H. Riesenfeld represented the reaction between hydrogen dioxide and an excess of chromic acid by the equation: $2CrO_3+3H_2O_2=Cr_2O_3+3H_2O+3O_2$ with the intermediate formation of a $Cr_2O_9$-oxide: $2CrO_3+3H_2O_2=Cr_2O_9+3H_2O$ followed by $Cr_2O_9=Cr_2O_3+3O_2$; and with the hydrogen dioxide in excess, $2CrO_3+2H_2O_2=2CrO_4+2H_2O$ followed by $2CrO_4+5H_2O_2=Cr_2O_3+5H_2O+5O_2$, or else according to $2CrO_3+7H_2O_2=Cr_2O_{13}+7H_2O$ followed by $Cr_2O_{13}=Cr_2O_3+5O_2$. H. E. Patten argued that it is the hydrogen not the chromium which forms a higher peroxide. He said:

> When a sat. soln. of potassium dichromate is cooled to $-16°$ and treated with 2 per cent. soln. of hydrogen dioxide at the same temp., a white, solid substance separates and the soln. turns blue. If a cold sat. soln. of sodium acetate is added to this soln., it assumes the lake-colour of chromous acetate, and if left for half an hour the green colour of chromic acetate appears. Solid chromous acetate may be obtained by extracting the blue soln. with ether and adding sodium acetate to the blue ethereal soln. The electrical conductivity of the blue ethereal soln. of "chromous oxide" is less than $2\times10^{-8}$ at 0°. The simplest explanation of these facts is said to be that chromic acid is reduced to the chromous state by hydrogen dioxide, and a higher oxide of hydrogen is produced.

This hypothesis, said K. A. Hofmann and H. Hiendlmaier, is untenable because much oxygen is evolved when hydrogen dioxide is mixed with chromic acid, and chromous salts are rapidly oxidized even by air, and they decompose water.

E. H. Riesenfeld pointed out that in the observations just indicated it is assumed

that only one chemical individual is concerned in the reaction when either the hydrogen dioxide or the chromic acid is in excess. Actually, several products are probably produced, and these are all prone to decomposition. Hence, the term **perchromic acid** applied to the blue product does not necessarily refer to a chemical individual. H. Moissan tried to isolate the blue compound by evaporating the ethereal soln. at −20°; he obtained a deep indigo-blue, oily, liquid with a composition corresponding with $CrO_3.H_2O_2$. E. Péchard added baryta-water to a well-cooled soln. of chromic acid containing an excess of hydrogen dioxide and obtained a brown precipitate approximating $BaCrO_5$, but which O. Wiede regarded as a mixture of barium chromate and dioxide. C. Häussermann treated a mush of chromium hydroxide and water with sodium dioxide at 10°-20°, and obtained reddish-brown, efflorescent crystals, $Na_6Cr_2O_{15}.28H_2O$. The subsequent observations of O. Wiede, E. H. Riesenfeld and co-workers, and K. A. Hofmann and H. Hiendlmaier have shown that the following derivatives of the oxidation products of chromic acid can be recognized:

*Compounds of the type: $R_3CrO_8$, or the red perchromates* or **triperchromates.**—E. H. Riesenfeld and co-workers discovered that these compounds are formed when an alkaline soln. of chromic acid is treated with 30 per cent. hydrogen dioxide. For example, the ammonium salt, $(NH_4)_3.CrO_8$, is prepared as follows:

A mixture of 50 c.c. of 25 per cent. ammonia, 25 c.c. of 50 per cent. chromic acid, and 75 c.c. of water is cooled until ice begins to separate; 25 c.c. of 30 per cent. hydrogen dioxide is added, drop by drop, with constant shaking and keeping the temp. below 0°. The soln. becomes at first reddish-yellow, and then brownish-black, and in one or two hours, crystals of the ammonium salt separate out. These are washed with 95 per cent. alcohol until the runnings show no coloration due to chromic acid. The salt is dried with ether, or on a porous tile. The sodium and potassium salts can be obtained in an analogous manner.

The preparation of **ammonium triperchromate,** $(NH_4O.O)_3CrO_2$, or $(NH_4)_3CrO_8$, or *red ammonium perchromate,* has just been described. E. H. Riesenfeld and co-workers said that the salt forms reddish-brown, doubly refracting, octahedral crystals. The salt decomposes when heated to 40° forming ammonium chromate; and at 50° it explodes forming chromic oxide. It cannot be kept more than 2 days at ordinary temp. without losing oxygen. Percussion, or contact with sulphuric acid results in an explosion with the formation of chromic oxide dust. The salt forms a reddish-brown soln. with a little cold water, and, in the presence of a little alkali, it can be kept for a day without decomposition; when the soln. is boiled it forms oxygen and chromate, and this the more quickly, the smaller the conc. of the HO-ions. If the soln. be acidified, blue perchromic acid is formed, and this at once decomposes into oxygen and a chromic salt, without forming a chromate. The salt is insoluble in alcohol and ether, and is not attacked by the boiling liquids. Alcohol with more than 50 per cent. of water decomposes the salt at ordinary temp. with the formation of chromate and aldehyde, and in acidic soln. the chromate is reduced at the same time to a chromic salt. C. W. Balke showed that the salts are isomorphous with the corresponding pertantalates. The isomorphism between the pertantalates, percolumbates and perchromates was discussed by G. Böhm. E. H. Riesenfeld and co-workers prepared **sodium triperchromate,** $Na_3CrO_8$—possibly with $H_2O$—as previously indicated. The reddish-yellow plates are doubly refracting, and deliquescent. The salt cannot be satisfactorily dried; and it is preserved in an atm. sat. with water-vapour. It decomposes explosively at 115°. When dried, it loses oxygen and forms a yellow powder possibly $NH_3HCrO_8$. It is slightly soluble in cold water, and insoluble in alcohol and ether. E. H. Riesenfeld obtained in a similar manner **potassium triperchromate,** $K_3CrO_8$. The dark red prisms are doubly refracting and slightly pleochroic. The salt was kept for a month without decomposition; it does not decompose by percussion, and at 170°, it slowly gives off oxygen and forms the chromate. It decomposes explosively at 178°, or in contact with conc. sulphuric acid. The impure salt is explosive.

The salt is sparingly soluble in water, and insoluble in alcohol and ether. The f.p., and the electrical conductivity of the aq. soln. show that the salt is completely ionized.

(2) *Compounds of the type: $RH_2CrO_7$ or $RCrO_5.H_2O_2$, or the blue perchromates,* or **diperchromates.**—These compounds were discovered by O. Wiede. They are less stable than the red perchromates and are formed by the action of an alcoholic soln. of an alkali on the blue ethereal soln. of perchromic acid at −5° to −10°. K. A. Hofmann and H. Hiendlmaier obtained the compound by the action of, say, a soln. of ammonium chromate and nitrate on hydrogen dioxide; and E. H. Riesenfeld and co-workers, by the action of 30 per cent. hydrogen dioxide on an acidic soln. of a chromate—for example:

The ammonium salt, $(NH_4)H_2CrO_7$, is formed by mixing 100 c.c. of water, 5 c.c. of conc. hydrochloric acid, 10 grms. of ammonium chloride, 10 c.c. of 5 per cent. chromic acid, and 25 c.c. of 30 per cent. hydrogen dioxide. If in the preparation of the red perchromates, the mixture is treated with hydrochloric, oxalic or acetic acid, before the addition of hydrogen dioxide, the blue perchromates are formed.

O. Wiede, K. A. Hofmann and H. Hiendlmaier, and E. H. Riesenfeld and co-workers prepared **ammonium diperchromate,** $(HO.O)_2(NH_4O)CrO_2$, or $NH_4H_2CrO_7$, or *blue ammonium perchromate,* as just indicated. The bluish-black or violet crystals are pleochroic between pale reddish-brown and dark bluish-violet. If moisture be excluded, the salt can be kept some days without decomposition, but it gradually passes into ammonium dichromate. When rapidly heated, the salt burns with a hissing noise forming chromic oxide and nitrogen oxides. The salt dissolves in ice-cold water forming a violet-brown soln. which has a neutral reaction. The conc., aq. soln. rapidly decomposes with the evolution of oxygen, and the formation of ammonium dichromate; at a higher temp., the reaction proceeds more quickly still. Dil. sulphuric acid forms a blue soln. which quickly decomposes into oxygen and chromic sulphate. If a layer of ether be poured over the solid, or the ice-cold soln., and the liquid be acidified with sulphuric acid, the ether extracts the blue perchromic acid. The fixed alkalies act like water; with aq. ammonia, a gas is evolved and, with cold soln., the end-product is chromium triamminotetroxide. According to O. Wiede, the diperchromate is insoluble in alcohol, but according to E. H. Riesenfeld and co-workers, it is somewhat soluble in that menstruum. The salt is insoluble in ether, ligroin, and chloroform. Lead acetate, or barium chloride produces a violet-brown precipitate which soon gives off gas and forms the yellow chromate; silver nitrate gives a brownish-violet coloration which immediately forms reddish-brown silver chromate; ferric chloride gives a grass-green coloration which when heated, or allowed to stand, becomes yellow with the evolution of gas; with ferrous sulphate, gas is evolved and a yellow soln. is formed; copper sulphate is without action; and potassium permanganate forms a blood-red soln. which when acidified gives off oxygen, and deposits a manganese peroxide. O. Wiede, and E. H. Riesenfeld, prepared **potassium diperchromate,** $KH_2CrO_7$, in an analogous manner. The salt forms pleochroic prisms—red, and violet. The dark violet powder detonates a few degrees above 0°; the crystals are more stable, but they decompose at room temp. The salt dissolves in water, forming a brown soln. which, when warmed, gives off oxygen and forms potassium dichromate. Its reactions resemble those of the ammonium salt.

(3) *Compounds of the type: $HCrO_5$ with an organic nitrogen base,* or **monoperchromates.**—O. Wiede first prepared these compounds, which are blue or violet in colour, and assigned to them the formula $RCrO_3.H_2O_2$. E. H. Riesenfeld showed that they are to be regarded as complex salts of perchromic acid, $HCrO_5$, with an organic base—tetramethylammonium, $N(CH_3)_4CrO_5$, aniline, $HCrO_5.C_6H_5.NH_2$, pyridine, $HCrO_5.C_5H_5N$, piperidine, $HCrO_5.C_5H_{11}N$, or quinoline, $HCrO_5.C_9H_7N$. O. Wiede obtained them by the addition of the base to the blue ethereal soln. of perchromic acid cooled to 0°. E. H. Riesenfeld obtained the pyridine salt as follows:

A soln. of a gram of chromium trioxide in 100 c.c. of water is treated with 10 grms. of pyridine, and 25 c.c. of a 3 per cent. soln. of hydrogen dioxide at room temp. When the mixture is allowed to stand for a short time, blue crystals of $HCrO_5.C_5H_5N$ separate out.

O. Wiede prepared **tetramethylammonium monoperchromate,** $(CH_3)_4NCrO_5$, in violet, prismatic crystals, which form a brown soln. with water. It can be kept in the cold for some days. As previously indicated, complex salts were also prepared with aniline, pyridine, piperidine, and quinoline. The pyridine salt obtained by O. Wiede, K. A. Hofmann and H. Hiendlmaier, and E. H. Riesenfeld and co-workers furnished blue, rhombic plates, which were doubly refracting, and pleochroic. The salt is fairly stable when dry, but in moist air, it slowly decomposes forming chromic acid. It detonates with a small rise of temp., or by contact with sulphuric acid. Its general reactions are like those of the other perchromates.

(4) *Compounds of the type :* $CrO_4.3NH_3$, or **complex chromium tetroxides.**—These compounds were also discovered by O. Wiede, who also found that the 3 mols. of ammonia can be replaced by 3 mols of potassium cyanide indicating that the compound is chromium triamminotetroxide. E. H. Riesenfeld also prepared $2CrO_4.5KCy.5H_2O$, or $K_5[(CrO_4)_2(Cy)_5].5H_2O$ ; and K. A. Hofmann and H. Hiendlmaier, a compound with ethylene diamine, $CrO_4.C_2H_4N_2.2H_2O$, and one with hexamethylenetriamine, $CrO_4.C_6H_{12}N_4$. O. Wiede prepared the triamminotetroxide by shaking 100 c.c. of 10 per cent. hydrogen dioxide with a soln. of 10 grms. of chromium trioxide in 500 c.c. of water with 500 grms. of ether free from alcohol ; and then adding 50 c.c. of cold, conc. ammonia. The precipitate which forms can be recrystallized from aq. ammonia. K. A. Hofmann and H. Hiendlmaier obtained it by the action of hydrogen dioxide on an ammoniacal soln. of ammonium dichromate ; A. Wesch obtained the same product by treating ammonium chromate in a similar way ; and A. Werner added hydrogen dioxide to a cold mixture of a soln. of chromic acid and pyridine ; digested the precipitate in 25 per cent. aq. ammonia whereby the triammine was formed. E. H. Riesenfeld found that if red ammonium perchromate is treated with 10 per cent. aq. ammonia at 40°, the soln. furnishes acicular crystals and rhombic plates. These crystals are simply different habits of the same chemical individual, and do not represent two isomeric forms assumed to exist by K. A. Hofmann and H. Hiendlmaier. E. H. Riesenfeld recommended the following mode of preparation :

Add drop by drop 5 c.c. of 30 per cent. hydrogen dioxide to a mixture of 25 c.c. of 10 per cent. aq. ammonia and 5 c.c. of 50 per cent. chromic acid at 0°. When the liquid has been cooled by a freezing mixture for an hour, it is heated to 50° until the rapid evolution of gas has ceased, and the salt has nearly all dissolved. The filtered soln. is cooled to 0°, when brown needles of chromium triamminotetroxide separate out.

O. Wiede, K. A. Hofmann and H. Hiendlmaier, E. H. Riesenfeld and co-workers, A. Werner, and A. Wesch prepared **chromium triamminotetroxide,** $CrO_4.3NH_3$, as previously indicated. The salt appears in brown, doubly refracting prisms ; when rapidly cooled, the hot soln. furnishes rectangular plates. O. Wiede reported the axial ratios of the rhombic, pyramidal crystals to be $a : b : c = 1{\cdot}0076 : 1 : 1{\cdot}308$. K. A. Hofmann and H. Hiendlmaier said that there are $\alpha$- and $\beta$-forms respectively with prismatic and tabular crystals ; but E. H. Riesenfeld and co-workers showed that both forms have a sp. gr. 1·964 at 15°, and have identical physical properties ; and concluded that they are really the same chemical individual. When heated the triamminotetroxide detonates and becomes incandescent forming chromic oxide. Y. Shibata measured the absorption spectrum. Strong acids liberate oxygen and form chromic salts ; weak acids—*e.g.* acetic acid—do not change the crystals. E. H. Riesenfeld and co-workers added that the amount of oxygen developed depends on the conc. of the acid. Thus, with dil. acids, most of the oxygen is set free as a gas, and with conc. acids, fully half the oxygen remains in soln. as hydrogen dioxide. If the complex salt be dissolved in aq. ammonia, and then acidified, a transient blue coloration appears, oxygen is evolved, and a green chromic salt soln. is formed. When the complex salt is treated with fixed alkalies,

oxygen and ammonia are evolved, and chromate is formed. The triamminotetroxide dissolves in aq. ammonia forming a brown soln., and likewise also in water, but with partial decomposition. The compound is insoluble in all other solvents tried. When 0·1 grm. is covered with alcohol-free ether, and a few drops of dil. sulphuric acid are added, and the mixture shaken, oxygen is evolved and the ether acquires a blue colour. When treated with potassium cyanide, the triamminotetroxide forms $CrO_4.3KCy$; with ethylenediamine, $CrO_4.C_2H_8N_2.2H_2O$; and with hexamethylenetetramine, $CrO_4.C_6H_{12}N_4$.

The four types of compounds are closely related chemically; and they can be transformed one into the other. Thus, if an aq. soln. of $(NH_4)_3CrO_8$ is treated with an acid, oxygen is evolved, and $(NH_4)H_2CrO_7$ is formed as a blue soln. and precipitate. If an excess of pyridine be added to either of these salts, $HCrO_5.C_5H_5N$ is formed; and when any of these three salts is treated with an excess of ammonia, the most stable of all the perchromates is produced, namely the triamminotetroxide, $CrO_4.3NH_3$. These changes can be all regarded as a result of the addition or abstraction of hydrogen dioxide. The formation of these compounds by the action of hydrogen dioxide on an aq. or ethereal soln. of chromic acid is taken by E. H. Riesenfeld to mean that the blue soln. does not contain one chemical individual—the $HCrO_5$ of O. Wiede—but rather must it be supposed that *der Grundstoff* is $CrO_4$ associated with hydrogen dioxide to form $2CrO_4.nH_2O_2$, where $n$ is 1, 3, or 5. Thus, $2CrO_4+H_2O_2=2HCrO_5$; $2CrO_4+3H_2O_2=2H_3CrO_7$; and $2CrO_4+5H_2O_2=2H_2O+2H_3CrO_8$.

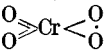
Other types have been reported. K. A. Hofmann and H. Hiendlmaier thought that the product obtained by the action of ammonium chromate on hydrogen dioxide in the presence of ammonia had the composition $(NH_4)_2CrO_6$ or $CrO_3(O.ONH_4)_2$, and that when treated with acetic acid it furnished blue $(NH_4)HCrO_6$ or $CrO_2(O.ONH_4)(O.OH)$; but E. H. Riesenfeld and co-workers showed that owing to defective analytical methods the compound with the assigned formula $(NH_4)_2CrO_6$ is identical with red $R_3CrO_8$; and that $(NH_4)HCrO_6$ is identical with O. Wiede's blue $(NH_4)H_3CrO_7$. H. G. Byers and E. E. Reid said that when the ethereal soln. of the blue perchromate is treated with potassium at −20°, hydrogen is evolved and the purplish-black precipitate produced has the composition **potassium perdichromate**, $KCrO_4$ or $K_2Cr_2O_8$. It is unstable, and rapidly decomposes with evolution of oxygen and the formation of potassium dichromate. By the addition of an alcoholic soln. of potassium cyanide to the blue soln., O. Wiede obtained a similar compound to which he ascribed the formula $KCrO_5.H_2O_2$. When the blue soln. is prepared without employing an excess of hydrogen dioxide, the compound obtained on the addition of potassium cyanide has the same composition as that produced by the action of potassium. The corresponding *sodium, ammonium, lithium, magnesium, calcium, barium, and zinc perdichromates* were prepared. It is inferred, therefore, that the blue ethereal soln. contains **perdichromic acid**, $H_2Cr_2O_8$. When the soln. is prepared in presence of an excess of hydrogen dioxide, it is probable that a more highly oxidized compound is also produced. These conclusions have not been confirmed.

J. A. Raynolds and J. H. Reedy obtained a soln. of red perchromic acid by the action of 30 per cent. hydrogen dioxide on freshly-precipitated chromic hydroxide at 0°; and **calcium perchromate**, $Ca_3(CrO_6)_2.12H_2O$, by adding 30 per cent. hydrogen dioxide to a sat. soln. of calcium chromate at −5° to 0°, or by mixing soln. of calcium acetate and red perchromic acid. The dry salt is a buff powder which explodes at 100°, and when treated with acid, it furnishes blue perchromic acid.

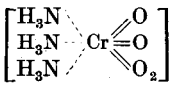
**The constitution of the perchromic acids** has been investigated by E. H. Riesenfeld and co-workers. Cryoscopic measurements of the $R_3CrO_8$-salts are in agreement with the simple formula, but, owing to deviations through decomposition, and ionization, the results are equally in agreement with the doubled formula. In benzene soln., the $HCrO_5$-compounds also have a mol. wt. in agreement with the simple formula; and a similar remark applies to the $CrO_4.3NH_3$-compounds in aq. soln. Measurements of the electrochemical eq. of chromium in these soln. were unsatisfactory. It can be assumed that the perchromates contain peroxidic oxygen or the bivalent $O_2$-group, because, although hydrogen dioxide cannot be detected among the decomposition-products, an alkaline soln. of gold chloride, or

potassium permanganate is reduced during the change. These reactions are characteristic of hydrogen dioxide.

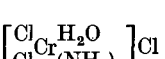
It has not been proved whether the chromium in the perchromates is sexivalent or of a higher valency. The chromium in the tetroxide may be sexivalent with a bivalent (–O–O–)-group—*e.g.*:



The triamminotetroxide can be formulated with the peroxidic oxygen occupying one position in the co-ordinate group:



This explains how (i) the compound decomposes into hydrogen dioxide, etc., when treated with acids; (ii) the treatment with an aq. soln. of potassium cyanide furnishes $CrO_4.3KCy$; (iii) the formation of complex chromium ammines observed by E. H. Riesenfeld; and (iv) the treatment with hydrochloric acid in acetic acid soln. furnishes chromic dichloroaquotriamminochloride



It is not so easy to deal with the other perchromates. Excluding H. G. Byers and E. E. Reid's perdichromates, the perchromate analogue of permonosulphuric acid, $H_2SO_5$, and perdisulphuric acid, $H_2S_2O_8$, have not been prepared, and consequently the arguments valid with the persulphates cannot, by analogy, be applied to the perchromates. If the formulæ be doubled, the red and blue perchromates can be regarded as derivatives of sexivalent chromium: where $(H_3CrO_8)_2$ becomes $(HO.O)_3:CrO.O.O.CrO(O.OH)_3$, and $(HCrO_5)$ becomes $HO.O.CrO_2.O.O.CrO_2.O.OH$.

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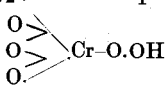
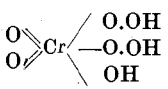
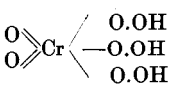
There is no serious objection to this mode of representing the composition of $H_3CrO_8$ perchromate, but mol. wt. determinations in the case of the $HCrO_5$-perchromate are against the doubled formula. Consequently the chromium probably has a valency higher than six. If nonivalent, $HCrO_5$ becomes $(O=)_4Cr.O.OH$; $H_3CrO_7$ becomes $(O=)_3Cr(OH)_2.O.OH$; and $H_3CrO_8$ becomes $(O=)_3Cr(OH)=(O.OH)_2$; and if septivalent,



Monoperchromic acid, $HCrO_5$.



Diperchromic acid, $H_3CrO_7$.



Triperchromic acid, $H_3CrO_8$.

The distinction between septivalent and nonivalent chromium turns on the number of peroxidic or —O.OH radicles. It is not possible to determine the number of peroxidic groups in acidic or alkaline soln. of the perchromate by means of potassium permanganate, because they decompose so rapidly. The red perchromates do not react with permanganate in strongly acid soln., but in alkaline soln. the amount of permanganate reduced increases with the alkalinity of the soln. to a maximum of 5·5 eq. Some peroxidic oxygen probably escapes without acting on the permanganate so that it is assumed that a mol. of the salt gives rise to 3 mols. of hydrogen dioxide. The escape of oxygen without reducing the permanganate is shown by the fact that no appreciable reduction occurs when the red perchromates are decomposed by strongly acidic soln. of permanganate, although oxygen is evolved; and by the fact that the blue perchromates are similarly decomposed in acidic or alkaline soln. of permanganate but only a trace of reduction occurs. This means that there are three peroxidic groups in $H_3CrO_8$; and this favours the hypothesis that *in the blue perchromates the chromium* is septivalent. This makes

the $H_3CrO_8$-acid, **triperchromic acid,** $(HO.O)_3CrO_2$; the $H_3CrO_7$-acid, **diperchromic acid,** $(HO.O)_2(HO)CrO_2$; and the $HCrO_5$-acid, **monoperchromic acid,** $(HO.O)CrO_3$. A. R. y Miro found that triperchromic acid, $H_3CrO_8$, instead of consuming 5 mols of oxygen per mol of dichromate in the reaction $2CrO_8'' + 12H^{\cdot} = 2Cr^{\cdot\cdot\cdot} + 6H_2O + 5O_2$ actually furnishes 4·6 to 6·5. This is explained by assuming the formation of an acid analogous to $HCrO_5$. Septivalent chromium is not in harmony with the position of chromium in the periodic table; and it makes chromium an exception to the other elements forming per-acids. If $HO.O.Cr(=O)_3$ be the hydrogen dioxide derivative of a chromic acid, $HO.Cr(=O)_3$, the acid is analogous with permanganic acid, $HO.Mn(=O)_3$. This analogy is supported by the isomorphism between the chromates and manganates; and between the chromium and manganese alums.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## § 20. Chromium Fluorides

C. Poulenc [1] prepared **chromium difluoride,** or **chromous fluoride,** $CrF_2$, by the action of hydrogen fluoride on red-hot chromium; and by the action of hydrogen fluoride on chromous chloride at ordinary temp. A. Mourlot obtained it by the action of hydrogen fluoride on chromous sulphide. G. Herrmann did not obtain good yields in the electrolytic reduction of chromic fluoride soln. K. Jellinek and A. Rudat found that the difluoride is produced by heating the trifluoride in hydrogen: $2CrF_3 + H_2 \rightleftharpoons 2CrF_2 + 2HF$. According to C. Poulenc, chromous fluoride forms a grey mass which consists of monoclinic crystals of sp. gr. 4·11. The salt is reduced by hydrogen at a red-heat. K. Jellinek and A. Rudat found that in the reaction $CrF_2 + H_2 \rightleftharpoons Cr + 2HF$, at the absolute temp. 873°, 973°, and 1073°, the values of $\log (p^2_{HF}/p_{H_2})$ are respectively −3·70, −3·02, and −2·56; those of $\log (p_{HF}/p_{H_2}p_{F_2})$, 33·12, 29·83, and 27·15; and $\log p_{F_2}$, −36·82, −32·85, and −29·50, where $p_{F_2}$ is the vap. press. of the difluoride. The heat of formation is 152 Cals. C. Poulenc observed that the difluoride is transformed into

chromic oxide when heated in air. It is sparingly soluble in water. Boiling hydrochloric acid dissolves the salt; and at a red-heat, hydrogen sulphide forms chromous sulphide. The salt is but slightly attacked by hot sulphuric acid, or dil. nitric acid; it is insoluble in alcohol; and forms chromic oxide and finally chromate when fused with alkali carbonates.

W. Traube and co-workers prepared **ammonium chromous fluoride,** $NH_4CrF_3.2H_2O$, from soln. of chromous acetate and ammonium hydrofluoride dissolved in very little water. The soln. gradually deposits a pale blue powder which is fairly stable in dry air, and forms a pale blue soln. with water. Dil. nitric acid oxidizes it with the evolution of nitrogen oxides. They also prepared **potassium chromous fluoride,** $KCrF_3$, in an analogous manner.

If dry chromic oxide, not previously calcined, be treated with an excess of hydrofluoric acid, and the soln. evaporated to dryness and strongly heated, **chromium trifluoride,** or **chromic fluoride,** $CrF_3$, is formed. H. St. C. Deville obtained it by passing hydrogen fluoride over a mixture of fluorspar and chromic oxide heated to redness in a carbon tube; and C. Poulenc said that by heating anhydrous chromic chloride, hydrated chromic fluoride or amorphous chromic fluoride, to 1200° in a current of hydrogen fluoride, when crystals of anhydrous chromic fluoride are formed. The dark green, needle-like crystals were found by C. Poulenc to have a sp. gr. of 3·78, and to melt over 1000°. H. St. C. Deville said that the salt melts at a high temp., and volatilizes only a little at the m.p. of steel; it sublimes at the highest temp. of the gas-blowpipe, forming regular octahedra. C. Poulenc found that the salt sublimes at 1100°–1200°. A. Speransky found that the lowering of the f.p. in conc. aq. soln. corresponds with the existence of both simple molecules, $CrF_3$, and doubled molecules, $Cr_2F_6$. E. Petersen gave for the heat of formation in aq. soln., $Cr_2O_3+6HF_{aq.}=2CrF_{3aq.}+3H_2O+50{\cdot}3$ Cals. H. von Wartenberg gave $(Cr,\frac{3}{2}F_{2aq.})=171{\cdot}3$ Cals. for the anhydrous trifluoride. G. Magnanini studied the absorption spectrum; and A. Speransky found that the electrical conductivity of aq. soln. shows that only a small proportion of the salt is ionized. The soln. of the violet modification conducts electricity three times better than that of the green. G. Gore electrolyzed a conc. soln. of chromic fluoride acidified with hydrofluoric and hydrochloric acids, and found that the liquid became hot; no gas was liberated at the cathode, but chlorine and ozone were liberated at the platinum anode which was not corroded. C. Poulenc showed that the salt is reduced by hydrogen at dull redness. The heat of formation is 230·95 Cals. per mol—*vide infra*, the dichloride. Steam transforms chromic fluoride into chromic oxide. Chromic fluoride is insoluble in water, and alcohol; hydrogen chloride transforms it into chromic chloride; hot hydrochloric, sulphuric, and nitric acids attack chromic fluoride only a little; hydrogen sulphide converts it into black sulphide; and molten alkali nitrate or carbonate converts it into chromate. A. Costachescu prepared complex pyridine salts.

According to J. J. Berzelius, brown chromic chromate forms a rose-coloured soln. when treated with hydrofluoric acid; and the soln. dries to a rose-coloured salt which dissolves in water and gives a brown precipitate with ammonia. E. Petersen observed that if chromium, or hydrated chromic oxide be dissolved in hydrofluoric acid, and the soln. evaporated, there remains a green, crystalline mass, soluble in water. G. Herrmann studied the electrolytic reduction of soln. of chromic fluoride. A. Werner and W. Costachescu obtained the insoluble green *trihydrate*, $CrF_3.3H_2O$, or $[Cr(H_2O)_6]CrF_6$, by heating the hexahydrate with water on a water-bath. That part which becomes insoluble is the trihydrate. It is also formed by heating the hemiheptahydrate to 105°. C. Poulenc obtained the *hemiheptahydrate*, $CrF_3.3\frac{1}{2}H_2O$, by pouring an aq. soln. of the fluoride into hot alcohol. The salt is a green crystalline powder which can be obtained in small prisms by allowing the soln. to diffuse slowly into one another. It is soluble in water. A. Werner and W. Costachescu obtained another form of the hemiheptahydrate by double decomposition between the hexahydrated chloride and

ammonium chromium hexafluoride. The pale green, crystalline powder loses a mol. of water at 105°. This salt is represented by the formula $[Cr(H_2O)_6]CrF_3].H_2O$, and it is considered to be isomeric with the tetrahydrate, which is regarded as the monohydrated **chromic triaquotrifluoride,** $[F_3{\equiv}Cr{\equiv}(H_2O)_3]H_2O$, whose aq. soln. has an acid reaction, and does not give the reactions of fluorides. The electrical conductivities of a mol of the salt in 100, 500, and 1000 litres of water are, respectively, 22, 26·6, and 31·0. A. Loesche's analysis corresponds with $Cr_3F_8.11H_2O_4$, or $CrF_2.Cr_2F_6.11H_2O$. A. Hiendlmayr prepared **chromic aquopentamminotrifluoride,** $[Cr(NH_3)_5(H_2O)]F_3$, by the action of hydrofluoric acid on the corresponding hydroxide. If the yellow compound be allowed to stand in contact with its mother-liquor, it furnishes **chromic fluopentamminodifluoride,** $[Cr(NH_3)_5F]F_2$, as a flesh-coloured precipitate which dries to a carmine-red powder. R. Köpp obtained what he regarded as a *tetrahydrate*, from a soln. of hydrated chromic oxide in hydrofluoric acid, and he recommended it for use as a mordant. It was probably imperfectly dried hemiheptahydrate. A. Werner and W. Costachescu treated a soln. of 20 grms. of violet chromic nitrate in the smallest possible quantity of water, with a conc. soln. of 8·69 grms. of potassium fluoride, and washed the crystalline mass of violet *hexahydrate*, $CrF_3.6H_2O$, or **chromic hexaquofluoride,** $[Cr(H_2O)_6]F_3$. The salt was dried first by press. between bibulous paper, and afterwards in a desiccator for 3–4 days over conc. sulphuric acid. The salt loses 3 mols. of water at 60°–70° in 8 hrs., and more at a higher temp., and it then decomposes. The salt is sparingly soluble in water, and is hydrolyzed in aq. soln. The electrical conductivity, $\mu$ mhos, of a mol of the salt in $v$ litres at 18°, is $\mu=152{\cdot}1$ for $v=100$; $\mu=196{\cdot}5$ for $v=500$; and $\mu=223$ for $v=1000$—about half that of the violet chloride. The conductivity does not change with time. When treated with sulphuric acid, it forms chromic hexaquosulphate. When the moist crystals are kept, they pass into the *enneahydrate*, $CrF_3.9H_2O$, or $[Cr(H_2O)_6]F_3.3H_2O$. The conversion occurs spontaneously when the crystals are washed, or pressed slightly with a spatula. G. Fabris prepared the enneahydrate, by treating a soln. of violet chromic sulphate with ammonium fluoride—not in excess. When the salt is heated, water is evolved, and the residue is green. The violet crystals are sparingly soluble in water; and insoluble in alcohol, and in a soln. of ammonium fluoride; the soln. in hydrochloric acid is violet; that in potash-lye is green. F. Hein and co-workers, and R. Weinland and W. Hübner, studied some complexes with organic compounds. F. Pintus prepared the complex with pyridine, chromic tripyridinofluoride, $[CrPy_3F_3]$; and E. Wilke-Dörfurt and H. G. Mureck, **chromic hexantipyrinoborofluoride,** $[Cr(COC_{10}H_{12}N_2)_6](BF_4)_3$.

J. J. Berzelius prepared ammonium, potassium, and sodium chromium fluorides as green sparingly soluble powders, but he did not give an analysis. R. Wagner found that **ammonium chromium pentafluoride,** $(NH_4)_2CrF_5.H_2O$, is formed when ammonia is passed into an aq. soln. of chromic fluoride, and the product extracted with absolute alcohol. Emerald-green, octahedral crystals are formed by treating the product with hydrofluoric acid. A. Werner and A. Gubser represent this salt as *ammonium aquopentafluoride*, $[Cr(H_2O)F_5](NH_4)_2$. R. Wagner, A. Werner and W. Costachescu, and E. Petersen obtained **ammonium chromium hexafluoride,** $3NH_4Cl.CrF_3$, by mixing soln. of chromic and ammonium fluorides; H. von Helmolt, by the action of a hot soln. of ammonium fluoride on freshly precipitated chromic oxide; and G. Fabris, by warming violet chromic sulphate with an excess of ammonium fluoride. The green, octahedral crystals are freely soluble in water, and sparingly soluble in a soln. of ammonium fluoride. A. Werner and A. Gubser represent this salt by the formula $[CrF_6](NH_4)_3$. R. F. Weinland and co-workers prepared the guanidine salt, $[CrF_6]H_3.3CH_5N_3$. R. Wagner prepared **sodium chromium pentafluoride,** $2NaF.CrF_3.\frac{1}{2}H_2O$, as a green, sparingly soluble powder, from a mixed soln. of sodium and chromic fluorides. A. Moberg observed that a soln. of chromic fluoride gives a green precipitate when treated with potassium fluoride. O. T. Christensen, and R. Wagner prepared **potassium chromium**

**pentafluoride,** $2KF.CrF_3.H_2O$, in green crystals, insoluble in water, and soluble in conc. hydrochloric acid. O. T. Christensen, and C. Poulenc also prepared **potassium chromium hexafluoride,** $K_3CrF_6$, from a mixed soln. of chromic fluoride and potassium hydrofluoride, or by melting a mixture of these two salts, and extracting the mass with hydrofluoric acid. A. Duboin obtained crystals of the salt by adding chromic oxide or fluoride to molten potassium hydrofluoride. The green crystals of the complex salt have a sp. gr. 2·93 at 0°. The green crystals are insoluble in water, and are not decomposed by a boiling soln. of sodium carbonate. A. Duboin said that the crystals are freely soluble in nitric and hydrochloric acids. G. O. Higley prepared **copper chromium pentafluoride,** $CuCrF_5.5H_2O$, by evaporating a soln. of eq. molar proportions of copper and chromium fluorides in hydrofluoric acid; and recrystallization from hydrofluoric acid. The salt loses water at 200°. He also obtained **zinc chromium pentafluoride,** $ZnCrF_5.7H_2O$, in an analogous manner. F. Ephraim and P. Barteczko prepared **thallous chromium enneafluoride,** $3TlF.2CrF_3$, by evaporating a mixed soln. of chromic and thallous fluorides. It forms a green, crystalline powder.


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## § 21. Chromium Oxyfluorides

O. Unverdorben [1] prepared what was thought to be a higher chromium fluoride by distilling in a platinum or lead retort a mixture of equal parts of lead chromate and fluorspar and 3 parts of fuming sulphuric acid. H. Rose employed potassium dichromate instead of lead chromate. It was discovered by V. Oliveri, in 1886, that the product is not chromic fluoride at all, but rather **chromium dioxydifluoride,** $CrO_2F_2$. The bivalent $CrO_2$-radicle is sometimes called the chromyl-radicle, so that the compound is also named **chromyl fluoride.** W. P. Evans used O. Unverdorben's process; and C. L. Jackson and G. T. Hartshorn, and V. Oliveri, H. Rose's process. O. Ruff heated antimony pentafluoride and chromyl chloride and obtained a yellow gas thought to be chromyl fluoride. The red vapour of chromyl fluoride, said O. Unverdorben, produces severe oppression of the lungs; and J. B. A. Dumas found that when cooled, the vapour condenses to a red liquid. O. Unverdorben

observed that the vapour is decomposed by water with the evolution of heat forming chromic and hydrofluoric acids; and when exposed to air, it forms a yellow cloud, and deposits crystals of chromium trioxide. Chromyl fluoride combines with ammonia; it converts arsenic trioxide into arsenic trifluoride and chromium trioxide; boric oxide forms boron trifluoride and chromium trioxide; and silica and even glass form silicon tetrafluoride and chromium trioxide. Organic substances are destroyed by the vapour; alcohol and ether form chromium trifluoride; and F. Wöhler said that when the vapour is passed into absolute alcohol a brownish-green powder is deposited and heat is evolved. C. L. Jackson and G. T. Hartshorn found that benzoic acid is converted into difluobenzoic acid; and V. Oliveri, that toluene reacts as in the case of chromyl chloride, forming a black mass, which, with water, gives benzaldehyde. O. Unverdorben found that mercury slowly decomposes the vapour of chromyl fluoride; and W. P. Evans found that zinc or sodium reduces the vapour to chromium (*q.v.*).

L. Varenne treated a nitric acid soln. of ammonium trichromate with hydrofluoric acid, and obtained red, efflorescent crystals of **ammonium dichromyl tetrafluochromate,** $(NH_4)_2CrO_4.2CrO_2F_2$. The crystals attack glass; and they are decomposed by acids, forming hydrofluoric and chromic acids. If ammonium dichromate be used instead of the trichromate, L. Varenne obtained **ammonium chromyl difluochromate,** $(NH_4)_2CrO_4.CrO_2F_2$, which can be regarded as **ammonium fluochromate,** $NH_4CrO_3F$, the salt of a hypothetical *fluochromic acid,* $HCrO_3.F$. The red crystals change slowly when exposed to air; they attack glass; and are decomposed by heat. A. Werner [2] represented the salt by $NH_4[CrO_3F]$. A. Streng boiled potassium dichromate with conc. hydrofluoric acid, and on cooling the clear soln., obtained ruby-red crystals of **potassium fluochromate,** $KCrO_3F$. L. Varenne obtained the salt by a similar process; and A. Ditte, by cooling a hot soln. of potassium fluoride and chromic acid in eq. proportions. A. Streng, and L. Varenne said that the crystals become reddish-yellow and melt when exposed to air; they cannot be preserved in glass vessels; they melt when heated, forming a dark brown liquid, and at a red-heat lose 11 per cent. in weight; at a still higher temp. in glass vessels, oxygen is evolved and silicon tetrafluoride is formed. A. C. Oudemans said that the salt decomposes as in the analogous case of the chlorochromates. A. Streng, and L. Varenne found that the salt is soluble in water, and boiling water converts the salt into potassium dichromate and hydrofluoric acid. The salt can be recrystallized from a little water; with sulphuric acid it forms hydrofluoric and chromic acids; and with alkalies, potassium fluoride and chromate are formed. F. Olsson prepared **potassium dioxydifluochromate,** $KF.CrO_2F.H_2O$, as a yellowish-brown precipitate by adding an aq. soln. of $4CrO_3.Cr_2O_3$ to an excess of a soln. of potassium fluoride in 40 per cent. hydrofluoric acid at 0°. This is thought to be a complex containing quinquevalent chromium.

R. Weinland and H. Staelin prepared a series of fluochromates which are represented on the co-ordination theory by the formulæ $H[CrO_3F]$ in the simplest case, analogous to $H_2[CrO_4]$ for the chromates. The fluochromates are represented by pyridine, quinoline, guanidine and **tetramethylammonium fluochromate,** $[CrO_3F]N(CH_3)_4$; and by **silver fluochromate,** $Ag[CrO_3F]$, obtained as a dark red, sparingly soluble powder by mixing a soln. of chromic acid with hydrofluoric acid, and silver acetate. They prepared **thallous fluochromate,** $Tl[CrO_3F]$, in an analogous way as a brownish-yellow powder sparingly soluble in water. Comparing the formula, $H[CrO_3F]$, with those for the polychromic acids—*vide supra*—there follow:

$$H\left[\begin{array}{l}(CrO_4)\\ Cr\ O_2\\ F\end{array}\right]$$

Fluodichromates.

$$H\left[\begin{array}{l}(CrO_4)_2\\ Cr\ O\\ F\end{array}\right]$$

Fluotrichromates.

The **fluodichromates** are represented by ethylenediamine fluodichromate,

$H[Cr(CrO_4)(O_2)F].en$; and the **fluotrichromates** by pyridine and quinoline fluotrichromates. A. Hiendlmayr[3] prepared **chromic fluopentamminochromate,** $[Cr(NH_3)_5F]CrO_4$, from a conc. soln. of the fluoride and potassium chromate. R. Weinland and co-workers prepared complex salts of the fluoride with pyridine, *o*-toluidine, guanidine, and aniline.


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## § 22. Chromium Chlorides

F. Hein and co-workers,[1] and F. Pintus obtained evidence of the formation of a transient **chromium monochloride,** CrCl, in their study of the action of magnesium phenyl bromide on chromic chloride: $4Mg(C_6H_5)Br+3CrCl_3=Cr(C_6H_5)_4Cl+2MgBr_2+2MgCl_2+2CrCl_2$; followed by $4CrCl_2+4Mg(C_6H_5)Br=Cr(C_6H_5)_4Cl+3CrCl+2MgCl_2+2MgBr_2$—the initial evolution of hydrogen as attributed to the action of the monochloride.

A. Moberg prepared **chromium dichloride,** or **chromous chloride,** $CrCl_2$, by passing dry hydrogen over heated violet chromic chloride as long as hydrogen chloride is given off. If the temp. be too high, A. Moberg, W. Gregory, and J. J. Berzelius found that chromium is produced. The hydrogen must be freed from traces of oxygen: to do this, A. Moberg passed the hydrogen over heated spongy platinum, while E. M. Péligot scrubbed the gas with a soln. of stannous chloride in potash-lye. E. M. Péligot observed that it may be formed at the same time as the trichloride when dry chlorine is passed over a red-hot mixture of chromic oxide and charcoal. C. E. Ufer, H. Moissan, and I. Koppel obtained chromous chloride by passing hydrogen chloride over chromium at a high temp. T. Döring showed that the reaction, $2CrCl_3+H_2=2HCl+2CrCl_2$, is irreversible. H. Moissan also obtained chromous chloride by heating chromic chloride in the vapour of ammonium chloride; and A. Recoura, by dehydrating the hydrates at 250° in a current of nitrogen—W. A. Knight and E. M. Rich worked at 180° in vacuo. F. Wöhler observed that an aq. soln. of chromous chloride is formed by dissolving chromium in hydrochloric acid; H. Löwel, H. Moissan, and A. Recoura, by reducing a soln. of chromic chloride with zinc; and K. Someya, by reducing soln. of chromic salts with zinc- or lead-amalgam. G. Herrmann studied the electro-reduction of soln. of chromic chloride to chromous chloride and obtained the following yields at 50°–60°:

| | | | | | | |
|---|---|---|---|---|---|---|
| Current density | . . | 1 | 2 | 3 | 4 | 5 amps. |
| Efficiency { | Pt electrode . | 16 | 35 | 67 | 50 | 25 per cent. |
| | Pb electrode . | 95 | 81 | 65 | 45 | 25 ,, |

W. Traube and co-workers prepared conc. soln. of chromous chloride by the prolonged electrolytic reduction of aq. soln. of green chromic chloride, using lead plates as electrodes and employing a current desnity of 0·175 amp. per sq. dm. The electrolysis of chromous chloride soln., using an iron cathode, results in the formation of a cathodic deposit of metallic chromium mixed with chromium oxides.

W. Traube and A. Goodson protected the soln. from air during electrolysis by covering them with light petroleum; they found that the most favourable conditions for the economic reduction are the electrolysis of the violet chromic salts in moderately acid conc. soln., using a lead cathode, and a current density of about 2·5 amp. per sq. dm. The more common green salts, in aq. soln., require a greater expenditure of current than the violet salts, but they yield much more conc. soln. and are, therefore, more suitable in the end for the production, at any rate, of soln. rich in chromous salts but not entirely free from chromic salts. The same slower reduction of the green complexes is observed when soln. are treated with zinc. M. C. Taylor and co-workers found that in a two-compartment cell with a spiral, spongy lead cathode, and five graphite anodes, a soln. of chromic chloride is reduced to chromous chloride. With a total cathode surface of 1·24 sq. dm. and a current of 1·6 amps. a current efficiency of 96 per cent. may be obtained over the period required to reduce 87 per cent. of the chromium if the soln. is rapidly stirred and if the current is reduced when hydrogen commences to be evolved. With an unchanged current the efficiency is only 53 per cent. for the same amount of reduction. F. Hein and co-workers found that phenyl magnesium bromide reacts with chromic chloride, forming chromous chloride, $3CrCl_3+4C_6H_5MgBr=(C_6H_5)_4CrCl+2MgBr_2+2MgCl_2+2CrCl_2$; and that the reduction proceeds further, forming **chromium monochloride,** CrCl, thus, $4CrCl_2+4C_6H_5MgBr=(C_6H_5)_4CrCl+3CrCl+2MgCl_2+2MgBr_2$. H. Moissan said that if the aq. soln. be evaporated, it deposits crystals of the *hexahydrate;* but A. Recoura, and W. A. Knight and E. M. Rich observed that it is the *tetrahydrate* that is formed under these conditions—*vide infra.*

Analyses of the anhydrous salt were made by A. Moberg, H. Moissan, E. M. Péligot, and A. Recoura. K. Someya discussed the colour of chromous salt soln. Chromous chloride may furnish white pseudomorphs after chromic chloride; it may form white needles; or colourless radiating masses. F. W. Clarke and J. P. Grabfield gave 2·751 for the sp. gr. at 14°/4°; and W. Biltz and E. Birk, 2·878 at 25°/4°. For the mol. vol., *vide infra,* hydrated chromic chloride. A. Moberg said that the salt is readily melted. L. F. Nilson and O. Pettersson found the vap. density (air unity) to be 7·80 between 1300° and 1400°; 7·27 between 1400° and 1500°; and 6·22 between 1500° and 1600°. The theoretical value for $CrCl_2$ is 4·256. The decrease which occurs with a rise of temp. indicates that the dissociation of more complex molecules is approaching completion. A. Recoura gave for the heat of hydration: $CrCl_{2solid}\rightarrow CrCl_2.4H_2O_{cryst.}+16·6$ Cals.; and for the heat of soln., 18·6 Cals. K. Jellinek and R. Koop found for the reaction $Cr+Cl_2=CrCl_2$, 76·68 Cals. F. Allison and E. J. Murphy studied the magneto-optic properties. W. Hampe found that molten chromous chloride is an electrical conductor, and on electrolysis, chromium separates at the negative pole. H. Küssner found that a chromium anode in soln. of potassium chloride dissolves with different valencies between 2 and 6. At low temp. and small current densities, the valency approaches 6, but at higher temp. no conditions could be found which gave only one kind of ion. Similar results were obtained with alcoholic soln. of zinc chloride. S. Meyer gave $47\times10^{-6}$ mass units for the magnetic susceptibility; and R. H. Weber gave for the atomic magnetism 0·0182. B. Cabrera and S. P. de Rubies studied this subject. G. Breit and H. K. Onnes found that the order of the magnetic susceptibility is unchanged when the frequency of alternation of the magnetic field is increased to 369,000, for the value in the alternating field is 0·75 of the value for the direct field.

The reaction $CrCl_2+H_2=2HCl+Cr$ was studied by K. Jellinek and R. Koop. The anhydrous salt is stable in dry air, but it deliquesces in moist air and becomes green owing to oxidation. The autoxidation of soln. of chromous chloride in the absence of air with the development of hydrogen was studied by A. Moberg, H. Moissan, and A. Recoura. M. Berthelot observed that the change is accelerated by acids; and T. Döring, that it is accelerated by precipitated gold; and W. Traube

and co-workers, that it is accelerated by palladium salts. A. Asmanoff showed that the reaction is accelerated by platinum in the presence of hydrochloric acid; and with sulphuric acid the reaction is slower. The unimolecular reaction with 0·1*N*-HCl at 29·4° has a velocity constant of 0·0129; and with 0·1*N*-$H_2SO_4$, 0·0115. Without platinum the evolution of hydrogen with 10*N*- sulphuric acid cannot be detected, but it can be observed with hydrochloric acid. Ammonium chloride in *N*-HCl gives a measurable yield of hydrogen even when platinum is absent. The reaction proceeds more rapidly in ammoniacal soln., and is fastest in soln. containing ammonium sulphate. The speed of the reaction increases as the conc. of the ammonia increases. The reaction in ammoniacal soln. is accelerated by chromic salts. W. Traube and W. Lange found that the conversion of chromous to chromic salts is accelerated by a metal of the platinum group, or by a hydrogen acceptor, as well as by substances which cannot be regarded as hydrogen acceptors. The reaction is interpreted according to the scheme $Cr(OH)_2 \rightarrow Cr(:O).OH+H$. The reaction was studied by H. Wieland and F. G. Fischer. E. S. Hedges and J. E. Myers showed that the evolution of hydrogen in the autoxidation of chromous chloride in the presence of platinum may be periodic, chromous chloride dissolved in *water* with the evolution of much heat forming a blue soln. which rapidly turns green owing to the absorption of oxygen, and, according to E. M. Péligot, the formation of $Cr_2OCl_2$—a reaction which A. Recoura found to be attended by the evolution of 100·8 Cals. Soln. of chromous chloride were used by F. O. von der Pfordten, R. P. Anderson and J. Riffe, W. Manchot and J. Herzog, for the absorption of *oxygen* in gas analysis—*vide* **8**. 49, 1. A. Mailfert studied the action of ozone. Chromous chloride is transformed into chromic chloride by *chlorine*, and A. Recoura gave for the heat of the reaction $(CrCl_{2solid}, Cl_{gas})=39·4$ Cals.; $(CrCl_{2soln.}, Cl_{gas})=CrCl_{3green\ soln.}+51·4$ Cals.; and $(CrCl_{soln.}, Cl_{gas})=CrCl_{3violet\ soln.}+60·8$ Cals. G. S. Forbes and H. W. Richter dissolved chromous chloride in ice-cold 0·1*N*-HCl in an atm. of hydrogen or carbon dioxide free from all traces of oxygen. The mercury or platinum potential rose continuously to a maximum value which became constant after two days. If traces of oxygen are present, the potential fluctuated irregularly. When referred to the hydrogen electrode as zero, at 25°, $E=-0·400+0·065 \log (Cr'''/Cr'')$. The maximum potential with platinum was about 0·16 volt lower than with mercury, and hydrogen was evolved. G. Herrmann studied the electrolytic reduction of soln. of chromic chloride. If *hydrogen chloride* is passed for a long time into a conc. soln. of chromic chloride, cooled to 0°, a bluish powder of *chromous hydrochloride*, $3CrCl_2.2HCl.13H_2O$, is formed; it is stable at 0°, but decomposes at 20°. A. Moberg, and E. M. Péligot found that the blue aq. soln. gives a pale green precipitate with *potassium fluoride*, but no precipitate with *potassium bromide, or iodide*. V. Rothmund, and R. Stahn studied the reduction of *perchlorates* by chromous salts. E. M. Péligot obtained a black precipitate with *potassium sulphide*—it is insoluble in an excess of the alkali sulphide. *Potassium sulphite* gives a brick-red precipitate. A. Moberg said that *ammonia* gives a pale blue precipitate and a little hydrogen is evolved—the supernatant blue soln. becomes red in air—but E. M. Péligot said that no hydrogen is given off; and added that a mixture of ammonia and ammonium chloride gives a blue soln. which becomes red on exposure to air. W. Peters found that chromous chloride absorbs ammonia, forming ash-grey **chromous hexamminodichloride,** $CrCl_2.6NH_3$, and when this is kept in vacuo it forms a violet **chromous triamminodichloride,** $CrCl_2.3NH_3$. W. Biltz and E. Birk found that the sp. gr. of the hexamminodichloride is 1·392 at 25°/4°. F. Ephraim and S. Millmann discussed the stability of these salts; and W. Biltz and E. Birk, the mol. vols. K. Kraut described the formation of some chromous ammines—*vide infra*. W. Traube and W. Passarge prepared lilac-coloured **chromous dihydrazinochloride,** $CrCl_2.2N_2H_4$, by precipitation on adding a soln. of hydrazine hydrate to a soln. of the chloride. The precipitate is washed with water, alcohol, and ether, and dried over sulphuric acid. R. Stahn studied the reduction of *potassium azide* by chromous salts. W. Traube and W. Passarge found that

chromous salts reduce *nitrous* oxide in the presence of alkali hydroxide to nitrogen ; *nitric acid*, and *hydroxylamine* are reduced quantitatively to ammonia, but the reduction of *nitrous acid* to ammonia is not quantitative. For the action of *nitric oxide*, studied by G. Chesneau, J. Sand and O. Burger, and V. Kohlschütter, *vide* **8**. 49, 35. A. Moberg found that *sodium hydrophosphate* gives a blue precipitate ; and sodium carbonate gives a yellowish-green precipitate and the supernatant liquor becomes yellow. W. Traube and W. Passarge showed that soln. of chromous salts are gradually oxidized, especially in acidic soln., with the liberation of hydrogen : $2CrO+H_2O=Cr_2O_3+H_2$ ; in consequence, they are able in the presence of water to reduce compounds with double or triple linkages. Thus, they reduce *acetylene* to ethylene, but not *ethylene* to ethene ; maleic and fumaric acids are reduced to succinic acid in acidic and alkaline soln. ; *cinnamic and phenylpropionic acids* yield $\beta$-phenyl propionic acid with an alkaline suspension of chromous oxide ; and *benzaldoxime* is transformed into benzylamine. E. M. Péligot found that *potassium thiocyanate* gives no precipitate. R. Stahn studied the reduction of *thiocyanic acid*, and of *potassium cyanide*. R. Ripan discussed the hydrolysis of chromic salts by potassium cyanate. J. J. Berzelius found that potassium cyanide gives a white precipitate insoluble in excess; E. M. Péligot found that *potassium ferrocyanide* gives a yellowish-green precipitate ; and *sodium acetate*, red crystals of chromous acetate. R. Stahn studied the reduction of *chloroacetic acid* and of *oxalic acid ;* and A. Moberg found that *potassium oxalate* gives a grey bluish-green precipitate ; *sodium formate* has no visible action ; *potassium tartrate* has no action ; *sodium citrate* gives a violet-red precipitate which slowly dissolves ; *potassium succinate* gives a scarlet-red precipi tate ; *potassium benzoate*, a pale red precipitate ; and *sodium tetraborate*, a pale blue precipitate. R. Stahn studied the reduction of *benzaldehyde*. A. Moberg observed that *potassium hydroxide* gives a yellow precipitate, and, added E. M. Péligot, if kept out of contact with air it gives a brown precipitate of hydrated chromous oxide (*q.v.*) accompanied by the evolution of hydrogen. W. Traube and co-workers found that the precipitation of soln. of chromous salts by alkali-lye gives a mixture of hydrated chromous and chromic oxides in varying proportions. E. M. Péligot regarded chromous chloride as one of the most powerful of reducing agents. For instance, it gives a brown precipitate of chromic chromate when treated with *potassium monochromate ; cupric salt* soln. furnish first cuprous chloride, and afterwards with an excess of chromous salt, a red precipitate of cuprous oxide or copper ; E. Zinth and G. Rienäcker studied the electrometric titration of salts of copper, silver, and gold with chromous chloride. According to E. M. Péligot, gold is precipitated from a soln. of *gold trichloride*, and the reaction is accompanied by an evolution of hydrogen ; and *mercuric chloride* furnishes mercurous chloride. H. Brintzinger and F. Oschatz followed the electrometric titration of *molybdic acid* with chromous chloride down to the formation of tervalent molybdenum ; and H. Brintzinger and F. Rodis, alloys of tin and antimony, copper and tin, and bismuth and tin. N. H. Furman titrated chromous salts with soln. of ceric sulphate. E. M. Péligot found that *tungstic acid* is reduced to the blue lower oxide ; and H. Löwel obtained tin from a soln. of *stannous chloride*. E. Zinth and G. Rienäcker studied the electrometric titration of salts of mercury, bismuth, and iron with chromous chloride.

As indicated above, H. Moissan obtained what he regarded as a *hexahydrate* by evaporating aq. soln. of chromous chloride ; but A. Recoura, G. Baugé, and W. A. Knight and E. M. Rich showed that the product is the tetrahydrate, $CrCl_2.4H_2O$, and they recommended the following mode of preparation :

Chromous acetate is dissolved in conc. hydrochloric acid in vacuo, and the clear soln. is boiled down to dryness. If this distillation is too prolonged, or if it is interrupted overnight, the dark green isomeride is usually formed, whilst if the temp. rises above 51° after crystals have begun to appear, the product is pale blue or light green or white, but these are varieties of the blue isomeride, and are finally converted into the stable dark blue hydrate in presence of cold water. The blue crystals are washed by repeated decantation with pure acetone, and the final drying carried out with ether.

The blue crystals of the tetrahydrate readily absorb oxygen from air to form a greenish-black oxychloride. W. A. Knight and E. M. Rich showed that the blue crystals prepared in this way appear to undergo no alteration when left for many months, but, in spite of the high degree of purity of this chromous chloride (especially when it has been reprecipitated from sat. soln. by conc. hydrochloric acid), its soln., on exposure to the air, has a markedly disagreeable odour. Water, not hydrogen chloride, is evolved when the hydrated salt is heated in vacuo at 180°. T. Döring found that the transformation of soln. of chromous chloride into chromic chloride is catalytically accelerated by platinum, gold, silicic acid, etc. J. W. McBain also studied the catalytic decomposition in the presence of colloidal platinum. M. Prud'homme showed that chromous chloride is green in hot, conc. soln., although its cold, dil. soln. is blue, and hence, by analogy with the chromic salt, he inferred that two isomeric forms exist in aq. soln. J. W. McBain isolated a dark green chromous chloride which gave a green soln. with water, but the soln. soon became azure-blue. The change from a green to a blue soln. occupies only a few seconds in neutral soln. at ordinary temp., but in acidic soln. the change is so retarded that it may require weeks for its completion. If the change from blue to green were due to a partial hydrolysis resulting in the formation of a green $Cr(OH)^{\cdot}$-cation, then it is difficult to explain M. Prud'homme's observation that conc. hydrochloric acid favours the formation of the green colour. The assumption that the change is due to a partial dissociation resulting in the formation of stable $CrCl^{\cdot}$-cation which colours the liquid green is supported by W. A. Knight and E. M. Rich's observation that the presence of a large proportion of another chloride favours the green colour. Observations on the f.p. of the green and blue soln. show that it is probable that the blue soln. furnishes three ions: $CrCl_2 \rightleftharpoons Cr^{\cdot\cdot} + 2Cl'$, while the green soln., being less ionized, furnishes two ions: $CrCl_2 \rightleftharpoons CrCl^{\cdot} + Cl'$.

W. A. Knight and E. M. Rich showed that if water be pumped from the tetrahydrate at 50°, a mixture of pale blue *trihydrate*, $CrCl_2.3H_2O$, and light green dihydrate is formed, but when water is added, the light green hydrate becomes pale blue trihydrate. The flask and contents are then heated to 51°, and the pale blue trihydrate is quickly dried at ordinary temp. by evacuation through a phosphorus pentoxide tube. The light green *dihydrate*, $CrCl_2.2H_2O$, is formed when water is pumped from the tetrahydrate between 70° and 80°; evacuation at 100° has no further effect. The dark blue tetrahydrate is the stable form up to 38°, when it passes into the dark green tetrahydrate; but if the dark green tetrahydrate does not appear, the dark blue modification is stable up to 51°, at which it passes into the pale blue trihydrate; the dark green tetrahydrate is stable between 38° and 60°–70°, when it forms the light green dihydrate. The pale blue trihydrate is converted into the light green dihydrate at 84°–86°, and this, in turn, becomes the white anhydrous chloride at 113°–115°. Fig. 73 represents the relationship between, say, the vap. press. or the conc. of sat. soln. and temp. The metastable regions are represented by dotted lines. The observed vap. press., $p$ mm., with sat. soln. were

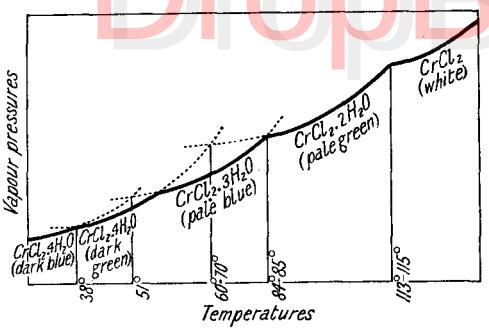


FIG. 73.—Diagrammatic Relation between Temperature and, say, Vapour Pressure of the Hydrated Chromous Chlorides.

| | 25° | 35° | 45° | 48° | 49° | 50° | 55° | 60° | 65° |
|---|---|---|---|---|---|---|---|---|---|
| $p$ . . | 2·9 | 8·0 | 19·0 | 25·0 | 27·6 | 28·8 | 39·7 | 56·0 | 78·4 |
| | $CrCl_2.4H_2O$ | | | | | $CrCl_2.3H_2O$ | | | |

There is a definite break in the curve at 49°, which is close to the 51° obtained by observations on the change of colour.

L. N. Vauquelin [2] evaporated a soln. of chromic oxide in hydrochloric acid to dryness and heated the product to expel the last traces of water. H. Rose said that the last traces of water cannot be expelled without forming chromic oxide which colours the mass green. J. J. Berzelius, and H. F. Gaultier de Claubry heated the residue to a high temp. when a large proportion sublimed as **chromic chloride,** or **chromium trichloride,** $CrCl_3$. H. Rose, and H. Löwel obtained the anhydrous chloride by heating the hydrated salt, obtained by evaporating an aq. soln. of the chloride, in a current of dry chlorine so that chromium trichloride sublimes. F. Wöhler found that heated chromium burns in chlorine forming violet chromium trichloride. H. Moissan said that the reaction occurs at 600°. J. Y. Johnson heated ferrochromium in chlorine gas with or without a reducing agent like carbon monoxide. Heat is required to start the reaction, but thereafter the temp. is controlled by varying the amount of chlorine so that iron chloride is sublimed. F. Wöhler, and C. E. Ufer also obtained this chloride by passing dry chlorine over an intimate mixture of chromic oxide and carbon. H. Moissan heated to 400° chromic oxide, which had not been previously calcined, in dry chlorine gas, and A. Vosmär applied the reaction to the opening up of ferrochromium for analysis. F. M. Jackson heated ferrochrome in chlorine at above 350° to volatilize the ferric chloride, and then to 650° to produce chromic chloride. R. D. Hall obtained the trichloride by heating chromic oxide in a current of sulphur monochloride vapour; C. Matignon and F. Bourion used a mixture of sulphur monochloride and chlorine with the chromic oxide at 400°; F. Bourion preferred sulphur dichloride. J. R. Mourelo considered this to be the best mode of preparation. E. Demarçay passed carbon tetrachloride vapour over chromic oxide to obtain chromic chloride—P. Camboulives recommended a temp. of 580°. G. Rauter observed that when chromium trioxide or a chromate is heated in the vapour of silicon tetrachloride, chromic chloride is formed; and A. Michaelis found that it is formed by the action of phosphorus trichloride on chromyl chloride. H. Quantin prepared chromic chloride by heating chromyl chloride in a current of carbon monoxide, or of carbon tetrachloride; and M. Prud'homme worked with the materials in a sealed tube at 200°. F. P. Venable and D. H. Jackson found that the chlorination of chromic oxide with a mixture of chlorine and carbon monoxide starts at 625°. P. Curie passed the vapour of carbon disulphide mixed with hydrogen chloride over heated chromic oxide; and J. J. Berzelius, C. E. Ufer, F. Serena, and L. R. von Fellenberg passed chlorine over heated chromium sulphide.

Chromic chloride, according to H. Rose, furnishes micaceous, puce or violet laminæ. Like talc, they leave a mark on the skin. The colour of chromic chloride becomes very much paler at liquid air temp. G. Natta found that chromic chloride crystallizes in the trigonal system—probably holohedral. The X-radiograms show that the unit cell has a side $a=4{\cdot}42$ A.; the axial ratio $a:c=1:1{\cdot}29$ or $1{\cdot}30$; and contains one mol. of $CrCl_3$ per unit cell; and the calculated sp. gr. is 2·71. On the other hand, N. Wooster found that the unit cell contains six molecules, the chlorine atoms being arranged in cubic close-packing, and the chromium atoms occupy octahedral positions. The parameter $a=6{\cdot}0$ A., and $c=17{\cdot}5$ A. A. Schafarik gave 3·03 for the sp. gr.; F. W. Clarke and J. P. Grabfield gave 2·757 at 15°/4°; and W. Biltz and E. Birk, 2·784 at 25°/4°. M. Crespi found the sp. gr. of the anhydrous salt heated at 100° in dry air is 2·916. It is difficult to dry the substance, and it absorbs water greedily. The absorption resembles the process of adsorption of gases by glass. The mol. vol. of the contained water increases with the quantity of water retained by the salt. L. F. Nilson and O. Pettersson found the *vapour density* (air unity) to be 6·13 at 1065°; 5·51 at 1191°; 5·42 at 1277°; 4·82 at 1347°; and 4·58 at 1350°–1400°, when the theoretical value for $CrCl_3$ is 5·478. Hence, the simple formula $CrCl_3$ represents the molecule in the state of vapour; above 1300°, dissociation sets in: $2CrCl_3 \rightleftharpoons 2CrCl_2+Cl_2$. A. Scott

confirmed these results. P. Fireman and E. G. Porter said that the dissociation, indeed, can be detected at 355°, for when an inert gas is passed over the chloride at that temp. and then through a soln. of potassium iodide, iodine is set free by the chlorine. F. Ephraim gave for the dissociation press., $p$, for $2CrCl_3 \rightleftharpoons 2CrCl_2 + Cl_2$, 205 mm. at 885°; 209 mm. at 902°; 415 mm. at 920°; 535 mm. at 930°; and 605 mm. at 933°. The results, however, are complicated by the volatility of the chromium chloride. H. Kopp gave 0·143 for the *specific heat.* K. Jellinek and R. Koop gave for the *vapour pressure:*

| | 700° | 800° | 900° | 1000° |
|---|---|---|---|---|
| P . . | 0·0187 | 0·0618 | 0·1845 | 0·366 atm. |

A. Recoura gave for the heat of formation: $CrCl_{2soln.} + Cl_{gas} = CrCl_{3soln.} + 56·7$ Cals. K. Jellinek and R. Koop gave for the reaction $2CrCl_2 + Cl_2 = 2CrCl_3 + 66·95$ Cals.; and for $Cr + 1·5Cl_2 = CrCl_3$, 110·18 Cals. O. Stelling studied the X-ray absorption spectrum; C. P. Snow and F. I. G. Rawlins, the colour; and P. Krishnamurti, the Roman effect. W. Hampe found that the *electrical conductivity* of the trichloride is very small. T. Peczalsky and J. Cichocky studied the effect of chromic chloride on the thermionic emission of copper. S. Meyer gave $34 \times 10^{-6}$ mass units for the *magnetic susceptibility* of chromic chloride at 18°; E. Feytis gave $44·1 \times 10^{-6}$ mass units; and for the atomic magnetism, R. H. Weber gave 0·00631. H. R. Woltjer, and H. R. Woltjer and H. K. Onnes observed that the susceptibility of chromic chloride decreases with the strength of the magnetic field at the temp. of liquid hydrogen; and for a given field strength, the susceptibility increases with falling temp. The observed data down to 64° K. follow the relation $\chi(T\text{-}32·5) = \text{constant}$, where $\chi$ denotes the susceptibility and $T$ the absolute temp. For the aq. soln., G. Quincke gave the magnetic susceptibility $40 \times 10^{-6}$ mass unit at 19°; S. Ishiwara gave $44·3 \times 10^{-6}$ mass unit at 18·5°; and G. Jäger and S. Meyer, $47 \times 10^{-6}$ mass unit at 19°.

A. Moberg, and E. M. Péligot observed that when *hydrogen* is passed over the heated chromic chloride, chromous chloride is formed, and J. J. Berzelius, and A. Moberg noted that at a higher temp. chromium is produced; K. Jellinek and R. Koop, that the reduction of chromic chloride by hydrogen proceeds $2CrCl_3 + H_2 \rightleftharpoons 2CrCl_2 + 2HCl$ between 416° and 510°, and $CrCl_2 + H_2 \rightleftharpoons 2HCl + Cr$ between 1021° and 1192°. V. N. Ipatieff and B. A. Mouromtseff found that a soln. of the chloride is reduced by hydrogen at 200 atm. press. H. Rose observed that when heated in *air*, chromic chloride is quietly reduced to the oxide. J. Y. Johnson converted the anhydrous salt into the hydrate without the aid of a reducing agent as catalyst by exposing an aq. suspension to the action of a cathodically polarized conductor, *e.g.* in a lead-lined iron vessel having a chromium anode and using a very low current density. The heat generated in the process enables a highly conc. soln. to be produced, which is filtered while hot and solidifies on cooling. H. Kunheim said that when heated in *water vapour*, chromic chromate is formed; and F. Bourion found that when heated in *oxygen* mixed with water vapour, chromic oxide is produced. For the solubility in water, *vide infra.* R. Schwarz and G. Meyer observed that anhydrous chromic chloride does not take up *hydrogen chloride.* A. Recoura found that if hydrogen chloride be passed for some days into a soln. of chromic chloride, the liquid gradually becomes brown or brownish-red, owing to the formation of a **chromic hydrochloride.** If ether be added, a green, unstable precipitate approximating $CrCl_3.HCl$ is formed. A. W. Cronander obtained a blue complex **chromic phosphoctochloride,** $CrCl_3PCl_5$, by the action of *phosphorus pentachloride* on chromic or chromyl chloride in a sealed tube at 150°. R. F. Weinland and C. Feige, and P. Pfeiffer prepared a complex with *antimony pentachloride,* namely, **chromium antimonioctochloride,** $CrCl_3.SbCl_5.10H_2O$, in green leaflets, and **chromium triantimoniododecachloride,** $CrCl_3.3SbCl_3.13H_2O$, in violet-grey needles. R. F. Weinland and H. Schmid obtained $Cr[SbCl_6]_3.15H_2O$, and also $[SbCl_6].CrCl_2.10H_2O$—*vide* antimony pentachloride, **9**. 52, 18. H. Rose said that puce-coloured

chromic chloride is extraordinarily resistant towards acids. According to L. R. von Fellenberg, boiling *hydrochloric*, or *nitric acid*, or *aqua regia* does not act on the chloride, but N. Bunge found that if a little sodium amalgam be added to dil. hydrochloric acid in which the trichloride is suspended, a green soln. and some chromium amalgam are formed. H. Rose observed that conc. *sulphuric acid* can be distilled from the puce-coloured chloride, but J. Pelouze added that with hot, conc. sulphuric acid, chlorine is slowly given off, leaving behind a green mass miscible with water. Molten *sulphur* was found by J. L. Lassaigne, and J. J. Berzelius, to furnish chromium sulphide; J. von Liebig noted that when heated in *hydrogen sulphide*, chromium sulphide is formed; H. Moissan said that *ammonium chloride* at a red-heat forms chromous chloride; A. Schrötter, that *ammonia* converts it into nitride. J. Persoz studied the action on chromic chloride. Neither aq. ammonia nor ammonia gas acts on violet chromic trichloride, but W. R. Lang and C. M. Carson found that the puce trichloride reacts with liquid ammonia forming a yellow powder from which water extracts **chromic hexamminochloride,** $CrCl_3.6NH_3.H_2O$, and also **chromic pentamminochloride,** $CrCl_3.5NH_3$; while W. R. Lang and E. H. Jolliffe obtained with *methylamine* the complex **chromic pentamethylaminochloride,** $CrCl_3.5(CH_3)NH_2$; and with *ethylamine*, **chromic pentaethylaminochloride**, $CrCl_3.5(C_2H_5)NH_2.H_2O$, whilst, at 60°, it forms **chromic tetraethylamminochloride,** $CrCl_3.4(C_2H_5)NH_2.H_2O$; *ethylenediamine* forms **chromic tetraethylenediaminochloride,** $CrCl_3.4C_2H_4(NH_2)_2.H_2O$; while *dimethylamine*, *diethylamine*, *trimethylamine*, *triethylamine*, *aniline*, *methylaniline*, and *dimethylaniline* have no action on chromic chloride. P. Pfeiffer obtained a salt with *pyridine*, namely, **chromic tripyridinochloride,** $CrCl_3.3C_5H_5N$—*vide infra*, ammines. G. Fuseya and K. Murata observed the complexes are formed with *glycine*; and H. Farl, with pyridine and chromic dichloroethylate. G. M. Bennett and E. E. Turner studied the reaction with *magnesium phenyl bromides*: $2CrCl_3+2(C_6H_5)MgBr=C_6H_5.C_6H_5+2CrCl_2+MgCl_2+MgBr_2$, etc. F. Hein obtained chromium phenyl bromide, $Cr(C_6H_5)_5Br$, as a product of this reaction. H. Rose found that *phosphine* produces the phosphide. I. Koppel said that the puce-coloured, anhydrous chloride does not dissolve in *ethyl alcohol*, but it does so if a piece of magnesium, zinc, or chromium be present, or if a trace of chromous acetate be added. According to L. C. A. Barreswill, when chromic chloride and alcohol are heated in a sealed tube, ethyl chloride is formed. F. Pintus, and I. Koppel obtained **chromium alcoholatochloride,** $CrCl_3.3C_2H_5OH$, in red needles—*vide infra*, ammines. P. A. Thiessen and B. Kandelaky examined these salts. P. Rohland said that puce-coloured chromic chloride is practically insoluble in absolute ethyl alcohol, *methyl alcohol*, *acetaldehyde*, and in *ether*. W. Eidmann found it to be insoluble in *acetone*; and H. Arctowsky, in *carbon disulphide*. A. Naumann said that the puce-coloured chloride is sparingly soluble in *methyl acetate*; and that the yellow form is slightly soluble in *benzonitrile*. L. Hackspill found that *calcium* reduces heated chromic chloride to chromium; F. Wöhler, that zinc, in molten potassium chloride, reduces it to chromium; L. R. von Fellenberg, and H. Rose said that the puce-coloured chloride is insoluble in dil. alkali-lye, and that it is decomposed by boiling conc. soln. of *alkali hydroxides and carbonates*; A. Geuther, that it reacts with chromium trioxide: $3CrO_3+2CrCl_3=Cr_2O_3+3CrO_2Cl_2$; and with molten *potassium dichromate*: $3K_2Cr_2O_7+2CrCl_3=Cr_2O_3+6KCrO_3Cl$. F. Wöhler obtained crystalline chromic oxide by fusing the trichloride with *sodium carbonate* and ammonium chloride.

According to N. Bunge, C. W. Vincent, and Z. Roussin, a slightly acidified soln. of chromic chloride or other chromium salt yields with **sodium-amalgam** an easily decomposable chromium amalgam. A. Commaille observed that **magnesium** precipitates only hydrated chromic oxide from a soln. of chromous or chromic chloride. K. Someya found that soln. of chromic salts are quantitatively reduced to chromous salts by **zinc-amalgam** or **lead-amalgam;** and C. Boulanger studied the reduction with **zinc** and with **aluminium**. According to T. Peczalsky, when a **copper** rod has its lower half surrounded by chromic chloride, cementation is

produced throughout its length, specially on the portion in contact with the salt. Metallic chromium was deposited on the rest of the rod, whilst rhombohedric copper crystals were found in the salt. If the rod was contained in exhausted "pyrex" tubes, surrounded by chlorides of copper, nickel, or chromium, deposits of copper were found to have penetrated the glass after 5–10 hrs. at 600°–800°.

H. Rose said that the anhydrous, puce-coloured chromic chloride is insoluble in cold water; and E. M. Péligot, that it is insoluble in boiling water. J. Pelouze added that it is very slowly soluble in cold water, but water at 150°–200° forms a deep green soln. H. Moissan also obtained an aq. soln. by heating the chloride with water in a sealed tube at 180°. According to E. M. Péligot, while chromic chloride is insoluble in cold water, yet, when in contact with chromous chloride, it dissolves with ease, heat being evolved, and a green soln. formed. The soln. has all the characteristics of chromic salts. A very small quantity, less than 0·000001 per cent. of chromous chloride, suffices to render chromic chloride soluble.

A. Moberg, and K. Drucker found that the dissolution of chromic chloride is facilitated by the presence of dil. acid and zinc; K. Drucker, aluminium, ferrous oxalate; a soln. of copper in cuprous sulphate, a soln. of arsenious acid and sodium hydrocarbonate or hydrogen in the presence of colloidal platinum at ordinary temp.; J. Pelouze, stannous, ferrous, or cuprous chloride, or sodium thiosulphate; V. A. Jacquelin, titanous chloride, or sulphur dioxide; H. Moissan, chromous bromide or iodide; and P. Rohland, hydrogen at 90°; and the following metals in contact with the chromic chloride have a decreasing order of activity in facilitating the dissolution of the salt: potassium, sodium, magnesium, aluminium, zinc, cadmium, tin, iron, nickel, lead, antimony, bismuth, copper, mercury, and silver—while platinum and gold are inactive. M. Bauck noticed that a piece of chromic chloride deliquescing on tinfoil forms a green spot presumably owing to the formation of a little chromous chloride by the reducing action of the tin. P. Rohland found that in methyl or ethyl alcohol, or acetone soln., the activity of chromous chloride in promoting the dissolution is less than in aq. soln.

E. M. Péligot, and J. J. Berzelius said that the chromous chloride acts as a contact catalyst; and L. C. A. Barreswill assumed that the chromous chloride forms with violet chromic chloride a double salt which decomposes into chromous chloride and a green soluble chromic chloride. H. Löwel supposed that the chromous chloride reduces the violet chromic chloride and at the same time is transformed into soluble chromic chloride, and the reaction continues anew. A. Recoura's hypothesis was somewhat similar to this. P. Rohland said that the action is not catalytic, but that it favours the dissolution of the chromic chloride by its reducing action. A considerable proportion of stannous chloride is required to do this work, and that indicates that the action is not a characteristic of catalyzed reactions. K. Drucker measured the rates of dissolution in the presence of various reducing agents—*vide supra*. He found that the rate is dependent upon (i) the nature of the reducing agent, (ii) its reduction-potential, increasing and decreasing with this, and (iii) its absolute conc. In the presence of a sparingly soluble reducing agent, the dissolution of the chromic chloride takes place provided that the agent is also present in the solid state. The function of the reducing agent does not appear to be entirely catalytic, but a reaction takes place between this and the chromic chloride. The dissolution is probably preceded by a slight reduction to chromous chloride, the catalytic influence of which is very great; only a small quantity of this can, however, be formed, since its potential in soln. of appreciable conc. is greater than that of hydrogen, whilst the potential in the soln. cannot rise above that of the reducing agent present. It has not been proved that the catalytic influence is wholly due to chromous chloride. E. Hein and co-workers studied some complexes with organic radicles.

**The hydrated chromic chlorides** are perhaps the most peculiar hydrated salts in inorganic chemistry. There are one tetrahydrate, three isomeric hexahydrates —violet, pale green, and dark green—and one decahydrate; and, as indicated below, the dehydration of the dark green hexahydrate furnishes a *hemihydrate*, $CrCl_3.\frac{1}{2}H_2O$, and a *hemitrihydrate*, $CrCl_3.1\frac{1}{2}H_2O$.

**The tetrahydrate,** $CrCl_3.4H_2O$.—L. Godefroy [3] prepared this salt by allowing

the dark green hexahydrate to stand over conc. sulphuric acid in vacuo. The pale green powder readily takes up 2 mols. of water to form the hexahydrate, with the evolution of heat—according to G. O. Higley—eq. to 83·96 Cals. A. Werner and A. Gubser showed that the tetrahydrate can also form double salts with 2 mols. of, say, alkali chloride. The aq. soln. of the tetrahydrate is identical with the aq. soln. of the dark green hexahydrate. A. E. Lindh studied the X-ray absorption spectrum. The mol. conductivity of the aq. soln., rapidly determined at 0°, is 49 at a dilution $v$=125—the conductivity increases to the value for the dark green hexahydrate after it has stood for some time. The arguments with respect to the constitution of the dark green hexahydrate (*q.v.*) are applicable to this salt. The 4 mols. of water are considered to be constitutional because they are not removed by drying. This means that the tetrahydrate can be regarded as **chromic dichlorotetraquochloride,** $Cr[Cl_2(H_2O)_4]Cl$.

**The dark green hexahydrate,** $CrCl_3.6H_2O$.—This salt was prepared by A. Moberg, and E. M. Péligot by evaporating the green soln. in vacuo; the green soln. used by the latter was obtained by dissolving the puce-coloured anhydrous chloride in water containing a trace of chromous chloride. P. Rohland prepared the salt in a similar way. H. Rose obtained the green soln. by boiling chromic acid in hydrochloric acid, or by dissolving hydrated chromic oxide in that acid; E. M. Péligot, by evaporating a mixture of lead chromate and hydrochloric acid, and extracting the chromic chloride with alcohol, or from the clear soln. obtained by digesting lead chromate with alcohol and hydrochloric acid; L. Godefroy sat. with chlorine a soln. of 3 parts of potassium dichromate in 7 parts of alcohol. The soln. was filtered through cotton-wool, and the filtrate distilled until it separated into two layers. On cooling, the green lower layer solidified to a mass of crystals which were purified by recrystallization from a small quantity of water. The crystals thus obtained are thin lozenge-shaped lamellæ which readily give off some of their water, but can be preserved in a closed vessel. A. Recoura, N. Bjerrum, and A. Werner and A. Gubser passed hydrogen chloride into a sat. soln. of chromic chloride prepared from chromium trioxide and hydrochloric acid, when crystals which have been variously described as green, or emerald-green needles or plates were obtained; R. F. Weinland and A. Koch, and A. Johnsen said that the crystals are six-sided, biaxial, monoclinic or triclinic plates; and J. Olie described them as doubly refracting, rhombic or pseudohexagonal plates. W. Biltz and E. Birk gave 1·835 for the sp. gr. at 25°/4°; and 145·2 for the mol. vol. The hygroscopic crystals were said by A. Werner and A. Gubser to have an intensely sweet taste. The analyses of A. Moberg, and A. Recoura gave rather different values for the amount of water of crystallization, but the analyses of E. M. Péligot, L. Godefroy, and A. Werner and A. Gubser agree with the formula $CrCl_3.6H_2O$. A. Werner and A. Gubser found that 2 mols. of water are readily withdrawn when the salt is confined over sulphuric acid in vacuo, but no more water is lost. On the other hand, J. Olie said that more than this amount of water can be removed because after long standing over sulphuric acid in vacuo at 15°, the surface of the salt becomes pale red. When heated for 6 hrs. at 100°, rather more than 4 mols. of water are expelled. The product is dark violet; it readily absorbs water from the atm.; and forms a soln. almost identical in appearance and behaviour with the original green salt. Some hydrogen chloride, however, was also given off under these conditions. N. Bjerrum observed that when the salt is kept for 4 months over phosphorus pentoxide, under 1 mm. press., there remains the red hemitrihydrate, $CrCl_3.1\frac{1}{2}H_2O$, which forms a yellowish-green soln. with water, changing to the violet-blue colour

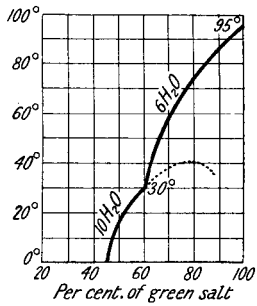


FIG. 74. — Solubility of Green Chromic Chloride in Water.

of the aq. soln. of green chromic chloride. J. Olie found that the natural m.p. of the salt—with 36 per cent. of the violet isomer—is 83°, and the true m.p. is over 90°—*cf.* Fig. 76; the salt can be heated slowly to 100° in vacuo without melting. J. Olie gave 2·66 Cals. for the heat of transformation to the violet isomer. H. de Bois and G. J. Elias measured the effect of temp., and of a magnetic field on the absorption spectrum of solid chromic chloride. The electrical conductivity of the soln. of the hemitrihydrate is at first less than that of the soln. of the hexahydrate, but it increases rapidly after a few minutes. If the green hexahydrate be heated very slowly to 155°, in a current of hydrogen chloride, there remains the hemihydrate, $CrCl_3.\frac{1}{2}H_2O$, as red powder. A. Recoura found that the green hexahydrate is freely soluble in water, so that at 15° the sat. soln. has 56·6 per cent. of the salt. J. Olie inferred that at 25° a sat. soln. has 50 per cent. of the green salt, but in the process of dissolution some violet salt is formed, and the change from the green to the violet salt (*vide infra*) goes on slowly until equilibrium is attained in about 10 days; this is accompanied by an apparent increase in the solubility of the salt, because the violet salt is rather more soluble than the dark green salt. Thus, at 25°, the percentage solubility, *S*, and the percentage proportions of dark green and violet salts in soln., are:

| Time . | 0·25 | 0·5 | 4·0 | 24 | 48 | 154 | 456 hrs. |
|---|---|---|---|---|---|---|---|
| *S* . | 58·36 | 59·39 | 63·27 | 68·50 | 68·42 | 69·01 | 68·58 per cent. |
| Green . | 91·70 | 87·43 | 75·20 | 62·36 | 59·10 | 57·16 | 57·38 ,, |
| Violet . | 8·30 | 12·57 | 24·80 | 37·64 | 40·90 | 42·84 | 42·62 ,, |

J. Olie also observed that the formation of the decahydrate introduces a complication, because there is a transition point near 30° when the system contains about 32 per cent. of the violet salt and 68 per cent. of the green salt. If a soln. sat. at a temp. below 32° is cooled, only the decahydrate separates out; but if sat. above 32°, both hexahydrate and decahydrate separate on cooling. A. Werner and A. Gubser also found that at room temp. the decahydrate changes to its equilibrium form very slowly. J. Olie represented his results by a diagram resembling Fig. 74. E. N. Gapon studied the speed of hydration and dehydration and of the passage of the green to the violet hydrate; and the mechanism of the charge, by L. Meunier and M. Lesbre. A. Recoura gave −0·04 Cal. for the heat of soln. of a mol of the green hexahydrate in 150 mols of water, but, according to J. Olie, this datum does not represent the heat of soln. of the green hexahydrate, but rather the heat of hydration to the decahydrate, and the heat of soln. of the decahydrate. O. Stelling studied the X-ray spectrum. E. Feytis observed that the magnetic susceptibility $23{\cdot}0\times10^{-6}$ mass unit is very little different from the value for the violet salt. R. H. Weber made observations on this subject. E. Feytis gave for the mol. susceptibility $6179\times10^{-6}$, and J. B. Elias, $6100\times10^{-6}$. N. Bjerrum found that the dark green hexahydrate is soluble in fuming hydrochloric acid; A. Werner and A. Gubser, that it is freely soluble in alcohol, sparingly soluble in acetone, and insoluble in ether; and P. Rohland, that it is nearly insoluble in ether, and freely soluble in methyl and ethyl alcohols as well as in acetaldehyde. The salt is largely ionized in methyl alcoholic soln., but the mol. wt. is normal in ethyl alcohol and in acetone soln. The formation of the salt was also studied by L. Meunier and M. Lesbre. From the properties of the soln., indicated below, A. Werner and A. Gubser regarded the dark green hexahydrate as **dihydrated chromic dichlorotetraquochloride,** $[CrCl_2(H_2O)_4]Cl.2H_2O$, with 2 masked chlorine atoms; the hypothesis is based on the behaviour of the salt on drying; on treatment with silver nitrate; and on the electrical conductivity of aq. soln.—*vide infra*. They also represented it by the formula $[(H_2O.Cl)_2Cr(H_2O)_4]Cl$.

**The pale green hexahydrate,** $CrCl_3.6H_2O$.—This salt was prepared by N. Bjerrum by pouring a hydrochloric acid soln. of chromic chlorosulphate into ether sat. with hydrogen chloride; and by boiling a soln. of 13·4 grms. of chromic dichlorotetraquochloride in 18 grms. of water for 10 mins., then sat. the soln. at 8°–10° with hydrogen

chloride; the filtered liquid was then poured into 200 c.c. of ether sat. with hydrogen chloride at 10°, while hydrogen chloride is passing through the liquid. The salt separates out when the soln. is allowed to stand, and it is washed with ether sat. with hydrogen chloride. The pale green hexahydrate is supposed to be present in aq. soln. containing the other two chlorides, and is said to be a maximum when the green dichlorotetraquochloride is dissolved in its own weight of water, and the soln. boiled for 10 mins.—*vide infra*. G. O. Higley obtained it by heating the violet salt to 70°; and by evaporating a soln. of the green chloride and hydrochloroplatinic acid, he obtained the salt $[Cr(H_4O_2)_5Cl]PtCl_6$. A. del Campo and co-workers obtained this salt by saturating with hydrogen chloride an aq. ethereal soln. of green chromic chlorosulphate, $[CrCl(H_2O)_5]SO_4.H_2O$. The pale green hexahydrate was also prepared by A. Werner and R. Huber, and by R. F. Weinland and T. Schumann. W. Biltz and E. Birk found the sp. gr. to be 1·760 at 25°/4°, and the mol. vol. 151·4. According to N. Bjerrum, the pale green, microcrystalline powder is very hygroscopic, and it slowly passes into the dark green salt. It is soluble in a mixture of equal vols. of fuming hydrochloric acid and ether forming a green soln., which, when poured into an excess of ether sat. with hydrogen chloride, deposits the pale green solid. The pale green hexahydrate forms a bluish-green soln. with water, and the colour slowly changes to bluish-violet; it is soluble in alcohol, and in acetone. Conc. sulphuric acid precipitates from the aged aq. soln., $CrClSO_4.6H_2O$. This behaviour of the salt together with its behaviour towards silver nitrate, and the conductivity of its aq. soln., suggests that the salt is **hydrated chromic chloropentaquodichloride,** $[Cr(H_2O)_5Cl]Cl_2.H_2O$, with one masked chlorine atom.

**The decahydrate,** $CrCl_3.10H_2O$.—L. Godefroy prepared this salt by placing a sat. soln. of the dark green hexahydrate in vacuo for several days at a temp. below 6°. A. Werner and A. Gubser obtained it by cooling, by means of a freezing mixture, a soln. of the dark green hexahydrate in half its weight of water; and J. Olie, by triturating the dark green hexahydrate with the theoretical proportion of water. L. Godefroy described the salt as forming green, triclinic crystals, which readily lose water. Over sulphuric acid, for example, they lose 4 mols. of water, and become opaque and friable. The salt melts slowly in its water of crystallization at a temp. above 6° or 7°. J. Olie found that when rapidly heated, the salt melts at 32°. This temp., however, is not a m.p., but rather a transition temp.—*vide* Fig. 74—A. Werner and A. Gubser found that the decahydrate is freely soluble in water, alcohol, and acetone. G. O. Higley found that the heat of soln. is zero; but in conc. soln., J. Olie found that the heat of soln. is negative. N. Bjerrum's observations on the extinction coeff. of the soln. are summarized in Fig. 75. The mol. conductivity of a fresh 0·00988*M*-soln. at 25° is 208·5 mhos, a value which is mean between those obtained for soln. of the dark green and the violet hexahydrates of the same conc. The hydrolysis constant, $K=8\times10^{-6}$ nearly, is about one-tenth the value for the violet salt. The conc. aq. soln., with conc. sulphuric acid, forms the chlorosulphate, $CrClSO_4.6H_2O$, or $[CrCl(H_2O)_5]SO_4.H_2O$. According to A. Werner and A. Gubser, the mol. conductivity, and the behaviour of the salt towards silver nitrate indicate that it contains two non-ionizable chlorine atoms; and it behaves like **hexahydrated chromic dichlorotetraquochloride,** $[Cr(H_2O)_4.Cl_2]Cl.6H_2O$. Two of the ten mols. of water can be replaced by metal chlorides. It is assumed that four of the mols. of the hexahydrate are doubled. The tetrahydrate, dark green hexahydrate, and the decahydrate all give aq. soln. of identical properties; and this when the soln. is freshly prepared before they have had time to undergo the slow changes indicated below. Consequently, deca-, hexa-, and tetra-hydrates are supposed to be similarly constituted: either $[Cr(H_2O)_4Cl_2]Cl$, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$, and $[Cr(H_2O)_4Cl_2]Cl.6H_2O$, or else

$$\left[\begin{matrix}H_2O.Cl\\H_2O.Cl\end{matrix}Cr(H_4O_2)_4\right]Cl \qquad \left[\begin{matrix}H_2O.Cl\\H_2O.Cl\end{matrix}Cr(H_2O)_4\right]Cl \qquad \left[\begin{matrix}Cl\\Cl\end{matrix}Cr(H_2O)_4\right]Cl$$

Decahydrate Hexahydrate. Tetrahydrate.

G. Quincke gave 1·2030 for the sp. gr. of a 20·8 per cent. soln. of $CrCl_3$ at 19°/4°. H. C. Jones and H. P. Bassett found the sp. gr. of soln. with $M$ mols of the salt per litre at 18° to be :

| $M$ . . | 0·05 | 0·1 | 0·2 | 0·4 | 0·6 | 0·9 | 1·5 | 2·25 |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. . | 1·0099 | 1·0142 | 1·0258 | 1·0507 | 1·0773 | 1·1117 | 1·1806 | 1·2631 |

E. Moles and M. Crespi gave 1·802 for the sp. gr. and 147·5 for the mol. vol. According to W. Biltz and E. Birk, the mol. vol. of $[CrCl_2(H_2O)_4]Cl.2H_2O$ is 145·2 ; of $[Cr(H_2O)_6]Cl_3$, 148·1, and of $[CrCl(H_2O)_5]Cl_2.H_2O$, 151·4. The mol. vol. of the most stable of the chromic salts, the dark green dichlorotetra-aquochromic chloride dihydrate, $[CrCl_2(H_2O)_4]Cl.2H_2O$, is 145·2, that of the grey hexa-aquochromic chloride, $[Cr(H_2O)_6]Cl_3$, is 148·1, and that of the least stable, the light green monochloropenta-aquochromic chloride monohydrate, $[CrCl(H_2O)_5]Cl_2.H_2O$, is 151·4. The mol. vol. thus falls with increasing stability, as for organic isomerides, the difference for each pair being 2 per cent. The mol. vol. of chromous chloride hexahydrate is 129·6, and this corresponds with a volume of 14·5 for each mol. of water. The mol. vol. of the water in the chromic chloride hexahydrates are 14·7, 15·2 and 15·7, respectively, and the chromous chloride thus corresponds with the dark green chromic salt and may be formulated $[CrCl_2(H_2O)_4].2H_2O$. H. Lessheim and co-workers discussed the electronic structure. J. E. Howard and W. H. Patterson found that the effect of the dark green salt on the critical soln. temp. of binary mixtures of water with butyric acid, isobutyric acid, and phenol, and of ethyl alcohol and paraffin, is nearly twice that due to the violet salt for concentrations up to 0·05$M$ ; above this conc., the difference becomes progressively smaller. H. C. Jones and H. P. Bassett found the lowering of the f.p. of aq. soln. of $M$ mol of the salt per litre to be :

| $M$ . | 0·05 | 0·1 | 0·2 | 0·4 | 9·6 | 0·9 | 1·5 | 2·25 |
|---|---|---|---|---|---|---|---|---|
| F.p. . | −0·268° | −0·510° | −0·030° | −2·160° | −3·610° | −6·30° | −15·0° | −33·0° |

DropBooks

Measurements were also made by G. Marchetti, and A. Werner and G. Gubser. The general results correspond with a mol. wt. nearly half the theoretical value 266·6. J. R. Partington and S. K. Tweedy observed that violet soln. of hexahydrated chromic chloride have a higher viscosity than analogous green soln., as would be anticipated from A. Werner's formulation of these salts. A. Recoura gave for the heat of the reaction ($CrCl_{3\text{green soln.}}$.$3NaOH_{soln.}$) = 31·5 Cals. at 10°, and the precipitated hydroxide dissolves in hydrochloric acid with the evolution of 20·7 Cals., or 20·6 Cals. according to E. Petersen ; the resulting soln. is blue.

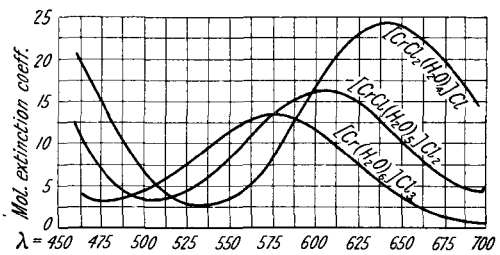


FIG. 75.—Molecular Extinction Coefficients of Solutions of the Chromic Chlorides for Light of Different Wave-lengths.

A. Piccini observed that the raising of the b.p. in methyl alcohol corresponds with a mol. wt. of about 50 ; in ethyl alcohol, 228 ; and in acetone, 271 ; the theoretical value is 266·6. F. Jost also obtained a mol. wt. of 33·2 in methyl alcohol. A. Recoura said that soln. appear green by reflected light, and red by transmitted light ; they found an absorption spectrum with a single green band ; a candle-flame viewed through such a soln. appears green ; but after the soln. has stood for 10 days a red band appears, and the flame finally appears to be reddish-violet. W. N. Hartley found that when anhydrous chromic chloride is dissolved in water, two kinds of salt are formed, one of which is precipitated by ammonium oxalate and the other not so. A soln. of the latter in thin layers at 20° shows a continuous

spectrum up to about $\lambda$=500 when bands appear at $\lambda$=704 to 685, and at $\lambda$=673 to 538. At 100°, the soln. is opaque. Observations were made by J. Formanek, W. Lapraik, J. M. Hiebendaal, J. L. Soret, H. W. Vogel, G. Magnanini, O. Knoblauch, A. Étard, H. C. Jones and J. A. Anderson, and H. C. Jones and W. W. Strong. N. Bjerrum found for the three hexahydrated chromic chlorides the mol. extinction coeff. illustrated by Fig. 75 for wave-lengths ranging from $\lambda$=450 to 700. The mol. extinction coeff., $k$, is defined by $I_o=Ie^{kml}$, where $I_o$ is the intensity of the incident light, and $I$ the intensity after traversing a layer, $l$ cm. thick, of a soln. with $M$ mols per litre. In an analogous way, A. Byk and H. Jaffe measured the limits of absorption for ultra-violet rays ranging from $\lambda$=440 to 220, and found for the green soln. of the chloride (eq. to 5 grms. of chrome-alum for 100 c.c.) an absorption band $\lambda$=490 to 409·1; and for violet soln. bands $\lambda$=433·1 to 400·0, and $\lambda$=400·0 to 385·5. H. W. Vogel measured the absorption spectrum of alcoholic soln.; and O. Stelling, the X-ray spectrum; H. C. Jones and W. W. Strong, the effect of the presence of various other salts in the soln. of chromic chloride. N. Bjerrum found the mol. electrical conductivity, $\mu$ mhos, of aq. soln. with $M$ mols per litre to be:

| $M$ | 0·00322 | 0·01074 | 0·00334 | 0·00998 | 0·0307 | 0·008 |
|---|---|---|---|---|---|---|
| $\mu$ | 103·1 | 97·9 | 88·6 | 83·0 | 79·5 | 49·0 |

Observations were also made by A. Werner and A. Gubser, H. C. Jones and H. P. Bassett, H. C. Jones and C. A. Jacobsen, and A. B. Lamb. According to A. W. Speransky, the mol. conductivity of the soln. of the dark green salt, is about one-third of that of the violet salt. This, said A. Werner and A. Gubser, shows that a smaller proportion of ions is formed by the ionization of the salt, so that while the violet salt furnishes four ions per mol, the dark green salt yields only 2 ions. As the soln. of the green salt is allowed to stand, the ionization proceeds further, owing to the partial transformation of the green into the violet salt—*vide infra*. F. Jost gave for the mol. conductivity of soln. of the green salt in methyl alcohol, at room temp.:

| $M$ | 11·55 | 15·48 | 28·7 | 55·5 | 129·9 |
|---|---|---|---|---|---|
| $\mu$ | 43·5 | 46·5 | 52·6 | 59·0 | 64·2 mhos. |

H. C. Jones calculated for the percentage degree of ionization, $\alpha$, and gave for the number of mols of water, $H$, in combination with a mol of the salt for soln. with $M$ mols of salt per litre:

| $M$ | 0·05 | 0·1 | 0·3 | 0·6 | 0·9 | 1·5 | 2·0 | 2·25 |
|---|---|---|---|---|---|---|---|---|
| $\mu$ | 52·7 | 46·9 | 38·1 | 31·2 | 25·6 | 16·9 | 11·6 | 9·6 |
| $H$ | 117·9 | 66·6 | 42·5 | 39·2 | 31·8 | 26·0 | 22·1 | 20·2 |

L. G. Winston and H. C. Jones gave for the conductivity, $\lambda$, and the computed percentage ionization, $\alpha$:

| $v$ | | 4 | 8 | 32 | 128 | 512 | 1024 | 2048 | 4096 |
|---|---|---|---|---|---|---|---|---|---|
| $\lambda$ | 0° | 86·30 | 104·53 | 130·03 | 162·34 | 188·46 | 200·21 | 214·48 | 229·73 |
| | 25° | 153·32 | 184·18 | 245·00 | 313·45 | 372·34 | 403·58 | 434·36 | 467·61 |
| | 35° | 199·10 | 243·55 | 319·15 | 393·62 | 465·10 | 504·31 | 543·02 | 586·16 |
| $\alpha$ | 0° | 37·6 | 45·5 | 56·6 | 70·7 | 82·1 | 87·2 | 93·3 | 100·0 |
| | 25° | 32·8 | 39·4 | 52·4 | 67·0 | 79·6 | 86·3 | 92·9 | 100·0 |
| | 35° | 34·3 | 42·0 | 55·0 | 67·9 | 80·2 | 86·9 | 93·6 | 100·0 |

H. M. Vernon estimated the degree of ionization from the colour of the soln. K. Hopfgartner's study of the transport numbers also led him to assume that the chromic ion is surrounded by a fairly large water sheath. F. L. S. Jones investigated the formation of complex anions in aq. soln.—*vide infra*, chromic sulphate. T. Murayasu studied the conductivity in soln. of the salt in glycine. N. Demassieux and J. Heyrovsky found that the polarization curve shows breaks at 0·7 and 1·35 volts, indicating that the electrochemical reduction occurs in two stages: $Cr^{\cdots}\rightarrow Cr^{\cdot\cdot}$, and $Cr^{\cdots}\rightarrow Cr$. The presence of an acid does not exert any influence on the

deposition potential, and this is taken to mean that $H^{\cdot}$-ions do not enter into the electrolytic process. It is also thought that the observations agree with the assumption that in conc. soln. the green chloride, $[CrCl_2(H_2O)_4]Cl.2H_2O$, is present; and that in dil. soln. the violet form, $[Cr(H_2O)_6]Cl_2$, predominates; and that it is easier to reduce the green complex than is the case with the violet.

According to E. Wiedemann, the atomic magnetism of chromium is about 42, when that of iron in ferric chloride is 42; and the result is independent of the anion associated with the chromium. Similar results were obtained by G. Jäger and S. Meyer. Observations on the subject were also made by E. Feytis, and R. H. Weber. E. Feytis gave for the mol. susceptibility $6181\times10^{-6}$; J. B. Elias, $5920\times10^{-6}$; and L. A. Welo found the susceptibility to be $22{\cdot}6\times10^{-6}$ mass unit.

The co-ordination theory of the constitution of the hydrated chromic chlorides, said I. Koppel, *findet ihre stärkste Stütze in dem verschiedenen Verhalten der Chloridlösungen bei der Fällung mit Silberion;* and A. B. Lamb and G. R. Fonda added that the application of the theory to the hydrated chromic chlorides is "perhaps the most striking exemplification of A. Werner's theory of molecular structure." The evidence lacks that decisive proof which would make the alternative hypotheses —*e.g.* the hydrolysis theory of their constitution—untenable. E. M. Péligot, and S. M. Jörgensen found that in the soln. of the dark green chloride two-thirds of the total chlorine is precipitated as silver chloride from newly prepared soln.; G. N. Wyrouboff said that five-sixths is so precipitated; while A. Werner and A. Gubser observed that at 0°, about one-third of the chloride is so precipitated—actually the amounts precipitated were rather greater than one-third. If the soln. are allowed to stand in contact with the silver salt, all the chlorine is ultimately precipitated as chloride. R. F. Weinland and A. Koch then showed that, using various silver salts as precipitants in the presence and in the absence of free acids, the proportion of chlorine precipitated depends on the nature and quantity of the particular silver salt employed. In the absence of acids, all the silver salts precipitated at least two-thirds of the chlorine as chloride; the presence of nitric acid diminished the proportion of precipitable chlorine; whereas silver salts of the weak acids—*e.g.* acetic, lactic, nitric or sulphuric acid—immediately precipitated all the chlorine. Silver salts of the strong acids—*e.g.* nitric, chloric, perchloric, or permanganic acid—did not precipitate all the chlorine as chloride, and the presence of strong acids suppressed the precipitation even more. A. Piccini also found that silver fluoride, like silver acetate, precipitated all the chlorine as chloride. He also found that a soln. of the dark green hexahydrate in ethyl alcohol or acetone gives up all its chlorine to an alcohol or acetone soln. of silver nitrate, whereas, with methyl alcohol soln., the results approximate to those obtained with water. J. Olie pointed out that R. F. Weinland and A. Koch used at least 3 eq. of silver salts and found at least two-thirds of the chlorine was precipitated; and he obtained similar results even with only 2·11 eq. of silver salt. J. Olie showed that the reaction $[CrCl_2(H_2O)_4]Cl.2H_2O\rightarrow[Cr(H_2O)_6]Cl_3$ is retarded or paralyzed by strong acids or $H^{\cdot}$-ions; and he explained the fact that whilst the silver salts of strong acids precipitate only part of the chlorine, and silver salts of the weak acids precipitate nearly all the chlorine, owing to the removal of $H^{\cdot}$-ions by the silver salts of the weak acids. The action of neutral salts, such as sodium and ammonium nitrates on precipitation by silver nitrate, is slight with small concentration, but a large amount of these salts greatly increases the proportion of chlorine thrown down. Strong acid at first cause a decrease in the proportion of chlorine precipitated until in certain concentrations only one eq. is affected; more conc. soln. cause an increase in the amount precipitated. Weak acids have a much smaller effect. The great effects of strong acids and neutral salts when present in considerable concentration is attributed to a direct exchange of the chlorine in the positive nucleus for other groups. A. B. Lamb said that the retarding action of the $H^{\cdot}$-ions on the isomeric change can be explained by assuming that one stage of the process involves the hydrolysis of the dark green chromic salt, say, $[CrCl_2(H_2O)_4]+Cl'+OH'+H^{\cdot}$

$\rightleftharpoons[CrCl_2(H_2O)_4]OH+H^{\cdot}+Cl'$. The chlorine in the central group may also be displaced by an analogous process of ionization. At equilibrium, the conc. of the base will be directly proportional to the conc. of the OH′-ion, and consequently also with water in excess, inversely proportional to the conc. of the H˙-ion; and if this hydrolyzed product be the compound which passes into the violet form by a slow reaction, the colour change will be proportional to the conc. of the OH′-ion, and inversely as the conc. of the H˙-ion. Hence the retarding action of H˙-ions on the colour change, and precipitation. The acidity of the $[Cr(H_2O)_6]^{\cdot\cdot\cdot}$-ion was found by J. N. Brönsted and C. V. King to be governed by the ionization: $[Cr(H_2O)_6]^{\cdot\cdot\cdot}\rightleftharpoons H^{\cdot}+[Cr(OH)(H_2O)_5]^{\cdot\cdot}$, and the variation of the ionization constant, $K$, with the conc. is in agreement with log $K$=log $K_a-Z_b\sqrt{\mu}$, where $\mu$ is the ionic strength; $K_a$, the acid ionization constant; and $Z$, the valency of the ion.

N. Bjerrum measured the degree of hydrolysis of soln. of chromic chloride from potential of the hydrogen electrode in the cell $H_2$ | $CrCl_{3soln.}$,$KCl_{sat.\ soln.}$ | 0·1$N$-calomel electrode. Assuming that $CrCl_3+H_2O=CrCl_2(OH)+HCl$, or more simply, $Cr^{\cdot\cdot\cdot}+H_2O=Cr(OH)^{\cdot\cdot}+H^{\cdot}$, the hydrolysis constant $K=[H^{\cdot}][Cr(OH)^{\cdot\cdot}]/[Cr^{\cdot\cdot\cdot}]$. At 25° it was found that for the soln. of the dark green salt $K$ varied from $3{\cdot}25\times10^{-6}$ to $4{\cdot}3\times10^{-6}$, and it is less marked than is the case with the soln. of the violet salt —*vide infra*. J. Olie also obtained a similar conclusion with respect to hydrolysis by showing that iodine is more rapidly separated from a mixture of potassium iodide and iodate (5 : 1) by soln. of the violet salt than is the case with soln. of the green salt. A. B. Lamb and G. R. Fonda obtained for the hydrolysis constant $K=1{\cdot}8\times10^{-6}$ to $2{\cdot}0\times10^{-6}$ calculated from the conductivities of soln. in different proportions of hydrochloric acid, and from the rate of transformation: $[Cr(H_2O)_4Cl_2]Cl\rightarrow[Cr(H_2O)_6]Cl_3$. J. Sand and F. Grammling studied the gradual hydrolysis of the green salt by sodium hydroxide. Observations were also made by H. G. Denham, and G. van Pelt.

H. de Sénarmont heated an aq. soln. of chromic chloride in a sealed tube and obtained chromic oxide. According to H. Löwel, a soln. of the green chloride in three to five times its weight of water, develops hydrogen when treated with granulated zinc in the absence of air. A blue soln. of chromous chloride is formed. If the soln. be acidified, the zinc acts more quickly. The soln. slowly deposits the chromium as oxychloride. Iron does not reduce the chromic chloride, but it forms hydrogen and chromium oxychloride. If the soln. be boiled with tin, in the absence of air, hydrogen is developed but the soln. remains green, and on cooling crystals of tin chloride are deposited.

A. del Campo obtained **chromic triaquotrichloride,** $[CrCl_3(H_2O)_3]$, by the action of hydrogen chloride on a soln. of the green chloride, $[CrCl_2(H_2O)_4]Cl.H_2O$, at 90° to 100°, under press.

A. Hiendlmayr prepared **chromic fluopentamminodichloride,** $[Cr(NH_3)_5F]Cl_2$, by the action of hydrochloric acid on a soln. of the corresponding fluoride. An aq. soln. of the yellow, four-sided plates gives no precipitate with potassium ferricyanide, but if acetone be added there is a green precipitate; hydrofluosilicic acid gives no precipitate; and sodium picrate gives a yellow precipitate consisting of fine needles.

**The blue, greyish-blue, or violet hexahydrate,** $CrCl_3.6H_2O$.—This salt was obtained by A. Recoura by heating a 50 per cent. soln. of the dark green chloride for some minutes at 80°, and then treating it with hydrogen chloride at 0°, when crystals of the violet hexahydrate separate out. A. Werner and A. Gubser used a similar process, boiling the soln. for an hour before treatment with hydrogen chloride at 0°. H. W. B. Roozeboom and J. Olie said that the precipitation of the violet salt by passing hydrogen chloride into soln. of the green salt previously heated to 100° is possible, because at the latter temp. the green salt rapidly passes into the violet salt with which it assumes a state of equilibrium, and the reverse change is slow enough to allow the precipitation of the violet salt at a temp. where the green salt is the stable state. A. del Campo and co-workers obtained the hexa-aquo-

chloride by the action of hydrogen chloride on a soln. of the violet sulphate at a low temp. G. O. Higley passed hydrogen chloride into a filtered soln. of 250 grms. of chrome alum in 1000 c.c. of conc. hydrochloric acid and 250 c.c. of water at 10°–15°. The crystals were dissolved in water and again precipitated with hydrogen chloride, and freed from the green isomer by washing with acetone. N. Bjerrum used the following process :

Hydrogen chloride was passed into a soln. of 40 grms. of enneahydrated chromic nitrate in 40 grms. of water and 40 c.c. of 38 per cent. hydrochloric acid, cooled by running water. The precipitate was washed on asbestos with fuming hydrochloric acid, mixed with 30 c.c. of conc. hydrochloric acid and again precipitated with hydrogen chloride. The mother-liquor was decanted from the crystals. The crystals were then washed with acid-free acetone, and dried over sulphuric acid in vacuo. The yield was 24·5 grms.—theoretical 26·7 grms.

Analyses in agreement with the formula $CrCl_3.6H_2O$ were made by A. Werner and A. Gubser, and R. F. Weinland and A. Koch—A. Recoura gave $CrCl_3.6\frac{1}{2}H_2O$. The colour of this form of chromic chloride ranges from grey to violet. According to J. Olie, they form six-sided, monoclinic prisms—R. F. Weinland and A. Koch added that lozenge-shaped plates are rare. W. Biltz and E. Birk gave 1·800 for the sp. gr. at 25°/4° ; and 148·1 for the mol. vol. J. Olie found the m.p. of the violet form to be 95°, and the m.p. curve of mixtures of the violet and dark green forms is shown in Fig. 76. The natural m.p.—**10**. 57, 5—of the green form is 83°, but that temp. really represents a mixture of the green form with 36 per cent. of the violet chloride. By extrapolation, the m.p. of the green chloride is over 90°. The salt can be slowly heated to 100° in vacuo without melting. Unlike the dark green salt, the violet chloride loses no water when confined over sulphuric acid at ordinary temp. S. Aoyama and co-workers studied the X-ray absorption and constitution. E. Feytis found the magnetic susceptibility to be $22{\cdot}2\times10^{-6}$ mass unit ; and R. H. Weber made observations on this subject. A. Werner and A. Gubser found that the violet salt is more hygroscopic than the dark green salt ; it is easily soluble in water. As in the case of the dark green salt, the solubility, $S$ per cent., of the violet chloride at 25° gradually increases with time owing to its passage into the green isomer. After a maximum of 72·22 per cent. has been attained, there follows a slow separation of the green salt (where the data are superscribed with an asterisk) :

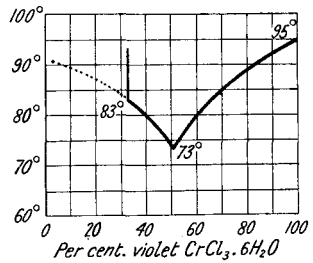


FIG. 76.—Melting-point Curve of the Dark Green and Violet $CrCl_3.6H_2O$.

| Time . | $\frac{1}{6}$ | 4·5 | 24 | 48 | 96 | 120 | 216 | 288 hours. |
|---|---|---|---|---|---|---|---|---|
| $S$ . | 61·99 | 63·19 | 63·88 | 66·16 | 70·68 | 72·22 | 68·95 | 70·01 per cent. |
| Violet . | 98·47 | 96·70 | 91·54 | 83·37 | 69·11 | 62·20 | 54·63 | 46·39 ,, |
| Green . | 1·53 | 3·30 | 8·46 | 16·63 | 30·89 | 37·80* | 45·47* | 53·61* ,, |

A. Recoura gave 12·02 Cals. for the heat of soln. per mol ; and for the heat of formation $(CrCl_3.6H_2O)=18{\cdot}6$ Cals. J. Olie estimated the heat of transformation from the dark green isomer to be −2·66 Cals. N. Bjerrum found that the violet salt passes into the green form particularly if moisture be present. J. Olie found the violet salt to be almost insoluble in absolute alcohol ; whereas A. Werner and A. Gubser said that it is easily soluble in alcohol, and insoluble in acetone. The behaviour of the salt on drying ; on treatment with silver nitrate ; and the conductivity of its aq. soln. are taken to be in agreement with the assumption that the violet salt is **chromic hexaquotrichloride,** $[Cr(H_2O)_6]Cl_3$, with no masked chlorine atoms. L. A. Welo gave $22{\cdot}4\times10^{-6}$ mass units for the magnetic susceptibility.

Aq. soln. of the violet hexahydrate are violet ; and H. Löwel, and A. Recoura obtained the violet soln. by adding barium chloride to a soln. of the violet sulphate.

A. Recoura observed that if hydrated chromic oxide be precipitated from the green soln., and then dissolved in hydrochloric acid, a violet soln. is obtained. J. Olie obtained the violet soln. by adding alkali salts to the green soln., or by shaking the green soln. with barium carbonate, and dissolving the gelatinous hydrated chromic oxide in acids. J. Olie, and N. Bjerrum found that the velocity of transformation of the green into the violet soln. is favoured by a high degree of hydrolysis of the soln.; and A. B. Lamb observed that sodium acetate accelerated the transformation from green to violet soln., while A. Recoura, and L. Godefroy showed that acids retard the transformation, and N. Bjerrum found that nitrates favour the green chloride. V. V. Kuriloff observed that the transformation from green to violet soln. is favoured by exposure to light. There appears to be a state of equilibrium between the green and violet hexahydrates in aq. soln. which is slowly attained. Thus, at 25°, J. Olie found that with a green soln. of the percentage conc., $C$, the percentage proportions of the two hexahydrates in the soln. when equilibrium is attained, are

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $C$ . | 3 | 19·70 | 22·72 | 34·70 | 50·19 | 57·57 | 68·50 per cent. |
| Violet . | 100 | 93·1 | 95·1 | 87·1 | 68·7 | 60 | 42·5 ,, |
| Green . | 0 | 6·9 | 4·9 | 12·9 | 31·3 | 40 | 57·5 ,, |

The same state of equilibrium is attained if a violet soln. be used, for in that case the violet salt slowly passes into the green salt until equilibrium is attained. It will be observed that the more dilute the soln., the greater the corresponding proportion of violet salt for the equilibrium state. Raising the temp. results in an increase in the proportion of green salt. Thus, at 84°,

| | | | | |
|---|---|---|---|---|
| $C$ . . | 53·7 | 55·8 | 60·8 | 80·25 per cent. |
| Violet . . | 68·10 | 48·51 | 48·15 | 37·35 ,, |
| Green . . | 31·90 | 51·49 | 51·85 | 62·65 ,, |

The speed of the transformation was measured by N. Bjerrum by measuring the change in the electrical conductivity or the change in the vol. of the soln.; and A. Heydweiller, by measuring the change in the conductivity, and in the sp. gr. of the soln. I. Koppel, and A. Werner and A. Gubser found that the velocity of transformation increases with the decreasing conc., and with increasing temp. Thus, with soln. containing a mol of chromic chloride in 125 litres of water, the molar conductivities $\mu$ mho, after the elapse of different periods of time, were

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time . . | 0 | 2 | 6 | 10 | 22 | 32 | 375 mins. |
| $\mu$ . . . | 110·9 | 134·8 | 166·1 | 181·3 | 211·9 | 225·4 | 307·4 mhos. |

at 25°, and at 0°, changing the unit from minutes to hours,

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time . | 0 | 0·5 | 6 | 18 | 24 | 73 | 88 hrs. |
| $\mu$ . | 56·6 | 60·0 | 81·2 | 106·6 | 115·9 | 149·7 | 164·2 mhos. |

and A. Heydweiller gave for soln. with 0·427 and 0·853 mols of the green salt per litre,

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Time . . | | 0 | 7 | 12 | 20 | 40 | 61 | 153 min. |
| $\mu$ { | 0·427 . | 42·75 | 57·81 | 62·33 | 65·60 | 67·53 | 67·67 | — mhos. |
| | 0·853 . | — | 79·85 | 84·3 | 89·0 | 96·0 | 98·0 | 99·7 ,, |

N. Bjerrum found the results did not agree with the velocity equation for monomolecular reactions; but the results were better represented by velocity equations for two consecutive, bimolecular reactions, on the assumption that the reaction involves the sequence of changes: $[Cr(H_2O)_4Cl_2]Cl \rightarrow [Cr(H_2O)_5Cl]Cl_2 \rightarrow [Cr(H_2O)_6]Cl_3$. If $x$, $y$, $z$ respectively denote the concentrations of these three salts, then $dx/dt = -k_1x$, and $dx/dt = k_2y$. It was found that at 25°, $k_1 = 0{\cdot}00272 + 0{\cdot}0000162/s$, and $k_2 = (31/s + 0{\cdot}005/s^2)10^{-7}$, where $s$ denotes the conc. of free hydrochloric acid. For soln. with $M$ mols of dark green chromic chloride, the

percentage conversion, $x$, at the time $t$ minutes, is as follows. With $M$=0·008 at 1° in aq. soln.,

| Time . . | 20 | 80 | 890 | 1490 | 4430 | ∞ mins. |
|---|---|---|---|---|---|---|
| $x$ . . | 2·5 | 8·3 | 38·8 | 32·9 | 80·1 | 100·0 mhos. |

For $M$=0·00322 at 25° in aq. soln.,

| Time . . | 2 | 6 | 30 | 90 | 120 | 210 mins. |
|---|---|---|---|---|---|---|
| $x$ . . | 15·7 | 30·8 | 61·3 | 82·0 | 86·6 | 93·9 mhos. |

For $M$=0·01074 at 25° in aq. soln.,

| Time . . | 3 | 9 | 30 | 90 | 180 | ∞ mins. |
|---|---|---|---|---|---|---|
| $x$ . . | 13·9 | 27·9 | 49·1 | 69·6 | 81·2 | 100·0 mhos. |

The addition of chlorides displaces the equilibrium: $Cr(H_2O)_6^{\cdots}+3Cl' \rightleftharpoons [CrCl(H_2O)_5]^{\cdot\cdot}+2Cl'+H_2O \rightleftharpoons [CrCl_2(H_2O)_4]^{\cdot}+Cl'+2H_2O$, in accord with the law of mass action, namely, from left to right. For $M$=0·01007 at 25° in the presence of 0·0100$N$-NaCl,

| Time . . | 3 | 9 | 33 | 68 | 451 | 1564 mins. |
|---|---|---|---|---|---|---|
| $x$ . . | 13·9 | 27·9 | 51·4 | 65·2 | 94·0 | 99·9 mhos. |

Similarly, hydrochloric acid favours the green chloride. For $M$=0·00965 at 25° in the presence of 0·01020$N$-HCl,

| Time . . | 20 | 60 | 100 | 290 | 2754 | 7140 mins. |
|---|---|---|---|---|---|---|
| $x$ . . | 3·8 | 11·4 | 18·0 | 38·4 | 76·7 | 94·5 mhos. |

The effect of temp. is very pronounced—between 1° and 25°, $k_1$ increases 4·8 times per 10°, and $k_2$, 4 times. M. E. Baldwin also studied the effect of neutral chlorides on the transformation, and found that the hydrogen-ion conc. of chromium chloride soln. is increased by the presence of neutral chlorides, although the total amount of acid hydrogen remains constant. When the salts are arranged in order of increasing effect, the following series is obtained: (KCl, $NH_4Cl$), NaCl, LiCl, $BaCl_2$. I. Koppel found that in alcoholic soln., the transformation increases with dilution and with temp. With a mol of the salt in 214·36 litres of alcohol at 0°,

| Time . . | 12 | 18 | 24 | 42 | 95 | ∞ min. |
|---|---|---|---|---|---|---|
| $x$ . . | 5·71 | 7·15 | 8·32 | 10·99 | 14·79 | 16·80 mhos. |

and with a mol of the salt in 273·9 litres of alcohol at 0°,

| Time . . | 10 | 30 | 81 | 141 | 231 | ∞ mins. |
|---|---|---|---|---|---|---|
| $x$ . . | 2·88 | 5·47 | 8·50 | 9·95 | 10·95 | 11·25 mhos. |

N. Bjerrum found that there is a marked contraction in vol. as the green soln. passes into the violet soln.; a mol of the green salt per litre, at 25°, changes the sp. gr. of the soln. from 1·125 to 1·139 as it passes into the violet. The sp. gr. of soln. of the violet hexahydrate have not been directly determined, although some observations of A. Heydweiller gave approximate values—*vide infra*. For the effect of the violet salt on the critical soln. temp. of some binary mixtures, *vide supra*, the dark green salt. Expressing conc. by the number of grams of the salt, $CrCl_3.6H_2O$, in 100 grms. of water, G. Marchetti found for the lowering of the f.p..

| $CrCl_3.6H_2O$ . | 0·9698 | 2·2345 | 5·0046 | 8·1770 | 12·5039 |
|---|---|---|---|---|---|
| F.p. . . | −0·240° | −0·0520° | −1·195° | −2·100° | −3·560° |

and the calculated values for the mol. wt. range from 60·7 to 81·6. A. Werner and A. Gubser also obtained mol. wts. 74·8 to 79·1 from observations on the f.p. The theoretical value is 266·6, so that it is inferred that the ionization of the salt furnishes 4 ions. F. Jost obtained mol. wts. of 54·7 and 60·3 from the b.p. of soln. of the violet chloride in methyl alcohol. A. Recoura gave for the thermal value of the reaction $CrCl_{3\,violet\ soln.}+3NaOH_{soln.}=Cr(OH)_3+3NaCl+22·2$ Cals., and

the precipitated hydroxide gives a blue soln. in hydrochloric acid and develops 20·7 Cals. The absorption spectrum of the soln. was discussed in connection with that of the dark green hydroxide, and there is a broad red absorption band in addition to the bluish-green band. N. Bjerrum gave for the molar electrical conductivity, $\mu$ mho, of aq. with $M$ mols of salt per litre, at 25°,

| $M$ | 0·00097 | 0·00195 | 0·00390 | 0·00779 | 0·01559 | 0·03118 |
|---|---|---|---|---|---|---|
| $\mu$ | 457·7 | 420·5 | 384·6 | 353·1 | 324·6 | 295·2 |

Measurements were also made by A. Werner and A. Gubser, A. Heydweiller, L. G. Winston and H. C. Jones, and E. J. Schaeffer and H. C. Jones. A. W. Speransky also found that the conductivity of the violet soln., at 25°, is $\mu_{25°}=324·5$ when that of the green soln. under similar conditions is $\mu_{25°}=126$. This is taken to prove that the violet salt furnishes more ions per mol than is the case with the green salt. F. Jost found for the conductivity of the violet salt in methyl alcohol,

| $M$ | 90·99 | 59·77 | 32·12 | 25·39 | 16·87 |
|---|---|---|---|---|---|
| $\mu$ | 97·7 | 90·1 | 78·7 | 74·1 | 67·7 mhos. |

K. Hopfgartner found the transport numbers for violet chromic chloride in 1·00, 0·32, and 0·075 eq. soln. to be respectively 0·318, 0·357, and 0·414, or extrapolating to zero concentration, 0·446. The mobilities of the ions are respectively 53, 49·5, and 46·3. These results indicate that the chromic ion is probably surrounded by a fairly large water sheath. N. Bjerrum found the constant of hydrolysis, as in the case of the dark green salt, and the percentage degree of hydrolysis, to be :

| | | 0° | 25° | 50° | 75° | 100° |
|---|---|---|---|---|---|---|
| $K$ | | 0·000022 | 0·000098 | 0·00034 | 0·00103 | 0·00264 |
| Hydrolysis | 0·1$M$- | 1·5 | 3·1 | 5·7 | 9·6 | 15·0 per cent. |
| | 0·001$M$- | 13·8 | 26·7 | 43·7 | 62·3 | 77·4 ,, |

A. B. Lamb and G. R. Fonda gave $K=1·58\times10^{-4}$ at 25°. N. Bjerrum's value was $K=0·98\times10^{-4}$ at 25°. H. G. Denham, and G. van Pelt made observations on this subject, for the violet hexahydrate is intermediate between the value for aluminium chloride $K=0·14\times10^{-4}$, and the value for ferric chloride, $25\times10^{-4}$. Observations were made by J. N. Brönsted and K. Volqvartz. K. H. Gustavson found that the addition of progressive amounts of sodium chloride to soln. of chromic chloride causes an initial increase in the H'-ion conc. represented by the value of $p_H$, and this is followed by a decrease with greater conc. of the sodium chloride. The latter effect is due to the increase in conc. of the chromium salt by hydration of the sodium chloride. The former change is most marked in dil. soln. of lesser acidity. It is supposed to be due to changes in the composition of the internal sphere in the chrome complex, different modifications of the basic aquo-chromic chlorides existing analogous to the normal chlorides $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2$, and $[Cr(H_2O)_4Cl_2]Cl$. The addition of sodium chloride will favour the formation of compounds with chlorine co-ordinately attached, and the increase in chlorine ions is evidenced by decrease in the electric charges of the cation and by an increase, in $p_H$. If sodium chloride is replaced by magnesium chloride, this effect is masked by the greater hydration tendency of the magnesium salt. The point at which precipitation occurs during addition of sodium hydroxide is not a function of $p_H$, but is proportional to the ratio of chlorine to chromium in the complex cation.

J. Sand and F. Grammling measured the velocity with which the violet hexahydrate liberates iodine from a mixture of potassium iodide and iodate, and found the results to be in agreement with the assumption that the molecule is $Cr_2Cl_6.12H_2O$, and not $[Cr(H_2O)_6]Cl_3$. H. W. Fischer found that the solubility of chromium hydroxide in an aq. soln. of green chromic chloride is not directly proportional to the conc. of the latter. A basic chloride is probably formed. From a soln. of chromium hydroxide in aq. chromic chloride, the former cannot be precipitated either by the addition of electrolytes or by the action of heat; part of it is supposed

to be in soln. in the colloidal form and part in the form of a compound containing chlorine. C. R. C. Tichborne said that, owing to hydrolysis, the green colour of the chromic salts is due to the formation of basic salts. The fact that the simplest way to convert the green soln. into a violet soln. is by boiling; that the change in colour of the green soln. is accompanied by the liberation of an acid, and the fact that incomplete precipitations with silver nitrate (and barium chloride) is a property common with elements known to be colloidal, led H. T. S. Britton to assume that the green soln. contain colloidal chromium hydroxide in which the cations of the colloidal electrolyte consist of chromium hydroxide associated with varying amounts of acid radicle. He showed that at 18°, 0·0133*N*-soln. of blue and green chromic chloride have respectively an e.m.f. of 0·467 and 0·409 volt against the *N*-calomel electrode; the H·-ion conc. are $p_H$=3·19 and 2·18; and the percentage hydrolysis 1·62 and 16·4. In the electrometric titration with sodium hydroxide, precipitation began when the e.m.f. were respectively 0·588 and 0·586 volt, when $p_H$=5·28 and 5·25; or when 1·07 and 1·43 eq. of NaOH per eq. of Cr had been added; and precipitation was complete when 2·78 and 2·15 eq. of alkali had been added. J. E. Howard and W. H. Patterson found that the effect of the violet and green salts on the critical soln. temp. of various mixtures is much greater than would be the case if the difference in the green and violet salts were due to the presence of basic, colloidal aggregates in the former. Colloids, *per se*, have usually a very small influence on the critical soln. temp. A. W. Ralston and J. A. Wilkinson found that soln. of the green and violet salts in liquid hydrogen sulphide are non-conducting.

A. Recoura passed hydrogen chloride into a soln. of chromic chloride for some days. The soln. turns brown and then red, presumably because of the formation of a soluble complex $CrCl_3.n$HCl. On adding ether, this complex is precipitated in unstable green needles. R. Schwarz and G. Meyer found that while anhydrous chromic chloride does not take up hydrogen chloride readily, the violet hexahydrated chloride forms some complexes; and the green salt $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ forms some complex chlorochromic acids at −50°, namely **tetrachlorochromic acid,** $CrCl_3.HCl.6{\cdot}5H_2O$, **pentachlorochromic acid,** $CrCl_3.2HCl.8{\cdot}5H_2O$, and **hexachlorochromic acid,** $CrCl_3.3HCl.10{\cdot}5H_2O$, as dark green compounds which decompose when heated. J. R. Partington and S. K. Tweedy obtained impure tetrachlorochromic acid, $CrCl_3.HCl.6H_2O$, as a precipitate by slowly saturating at 0° a conc. soln. of dark green chromic chloride mixed with an equal vol. of ether. It is washed with dry ether.

The hydrolysis of chromic chloride formerly represented by $CrCl_3+H_2O \rightleftharpoons Cr(OH)Cl_2+HCl$; $Cr(OH)Cl_2+H_2O \rightleftharpoons Cr(OH)_2Cl+HCl$; and $Cr(OH)_2Cl+H_2O \rightleftharpoons Cr(OH)_3+HCl$, is now represented by A. Werner, and P. Pfeiffer as involving the formation of hydroxyl-compounds in the stages:

$$[Cr(H_2O)_6]Cl_3 \rightarrow \left[Cr\begin{matrix}OH\\(H_2O)_5\end{matrix}\right]Cl_2 \rightarrow \left[Cr\begin{matrix}(OH)_2\\(H_2O)_4\end{matrix}\right]Cl \rightarrow \left[Cr\begin{matrix}(OH)_3\\(H_2O)_3\end{matrix}\right]$$

With increasing hydrolysis, the H·-ion conc. of the soln. also increases. According to N. Bjerrum, with ageing, or more rapidly with heating, the hydroxyl compounds suffer an internal change producing the so-called *ol-salts*, which in contact with acids, are more stable than the hydroxyl salts. The action is represented graphically:

$$2\left[(H_2O)_4Cr\begin{matrix}OH\\OH\end{matrix}\right]Cl_2 = \left[(H_2O)_4Cr\begin{matrix}OH\\HO\end{matrix}Cr(H_2O)_4\right]Cl_4$$

so that the molecular vol. of the salt in soln. increases and may assume the character of the colloid. When an acid is added to a hydroxyl compound some is consumed in reversing the change to form an aquo-compound [Cr—OH]+HCl=[Cr...$H_2O$]Cl, but with an ol-salt the first addition of acid simply increases the acidity of the soln.,

and thereafter gradually reforms the hydroxyl salt which then passes into the aquo-salt:

$$\left[(H_2O)_4Cr\begin{matrix}OH\\HO\end{matrix}Cr(H_2O)_4\right]Cl_4 \rightarrow 2\left[(H_2O)_4Cr\begin{matrix}OH\\HO\end{matrix}\right]Cl_2 \rightarrow 2\left[Cr(H_2O)_6\right]Cl_3$$

The resistance offered by the different chromium complex salts to this change depends on the nature of the complex radicles—chloride, sulphate, formate, oxalate, etc. With longer ageing, or heating, a more drastic, irreversible, internal change occurs, which, according to D. Balanyi, results in the formation of oxy-salts, a change which makes the mother-liquor more acidic, thus:

$$\left[H_2O_4Cr\begin{matrix}OH\\HO\end{matrix}Cr(H_2O)_4\right]Cl_4 \rightarrow \left[(H_2O)_4Cr\begin{matrix}O\\HO\end{matrix}Cr(H_2O)_4\right] \rightarrow \left[(H_2O)_4Cr\begin{matrix}O\\O\end{matrix}Cr(H_2O)_4\right]$$

The resulting product is not attacked by standing in contact with cold dil. hydrochloric acid.

E. Stiasny and O. Grimm found that the properties of chromic chloride soln. depend largely on whether the liquor is heated before being rendered basic, on the degree of basicity, on the heating or ageing after being rendered basic, and on ageing after heating. When a basic chromium chloride soln. is boiled for 5 mins. the $p_H$ value alters and only recovers after three days. It also decreases on ageing until it reaches 2·79 after four weeks; the addition of hydrochloric acid postpones the "ageing" effect. Heating before rendering the soln. basic causes chlorine to enter the chromium complex, but there is no chlorine in the complex after the soln. has been rendered basic and aged for a short time. The boiling of the soln. before rendering it basic encourages the formation of "ol" compounds; "ageing" has the same effect. Boiling is more effective in the formation of "ol" compounds and oxygen bridges after the liquor has been made basic than before. Heating increases the precipitation value both of normal and basic chromic chloride soln. owing to the formation of "ol" compounds which are less easily precipitable than the hydroxy-compounds. The heating effect is more pronounced with the more basic salts. Ageing diminishes the precipitation value of heated soln. of normal chloride which have not been heated, and of soln. of the basic salt which have been heated before and after rendering basic, but increases the value for basic soln. which have been boiled before rendering basic only. The dialytic properties of the different types of chromium chloride soln. are almost the same, showing that conversion into "ol" compounds does not result in the formation of large molecules unless the basicity exceeds 33 per cent. T. Murayasu found that the electrical conductivity of the soln. of chromic chloride is increased by adding glycocoll.

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## § 23. The Chromium Oxychlorides

The hydrolysis of chromic chloride, and the formation of some basic chlorides have just been discussed. N. Bjerrum[1] studied the titration of soln. of chromic chloride with sodium hydroxide, and calculated the $H^{\cdot}$-ion conc. from the potential measurements. The results with 0·1*M*-$CrCl_3$ and increasing proportions of 0·1275*M*-NaOH, at 17°, are illustrated by Fig. 77. When there is less than a mol of sodium hydroxide per mol of chromic chloride, the curve is steep, and the soln. remains clear; as soon as a mol of NaOH has been added, chromic hydroxide separates, and the soln. becomes turbid, and thereafter the $H^{\cdot}$-ion conc. increases slowly. So long as the soln. remains clear, the reaction is taken to be $Cr^{\cdot\cdot\cdot}+HOH=Cr(OH)^{\cdot\cdot}+H^{\cdot}$ for which the equilibrium constant $K_1=[Cr(OH)^{\cdot\cdot}][H^{\cdot}]/[Cr^{\cdot\cdot\cdot}]$, thereafter the reaction $Cr(OH)^{\cdot\cdot}+HOH=Cr(OH)_2^{\cdot}+H^{\cdot}$ sets in, and for this, $K_2[Cr(OH)_2^{\cdot}][H^{\cdot}]/[Cr(OH)^{\cdot\cdot}]$; and later on there is the reaction $Cr(OH)^{\cdot\cdot}+2H_2O=Cr(OH)_3+2H^{\cdot}$, for which $K_3=[H^{\cdot}]^2/[Cr(OH)^{\cdot\cdot}]$. He found for the hydrolysis constants of the green salt at 25°, $3{\cdot}8\times10^{-6}$; and of the blue salt at 0°, 17°, and 25°, $K_1\times10^4=0{\cdot}22$, 0·62, and 0·98 respectively; at 0° and 17°, $K_2\times10^4=0{\cdot}0025$ and 0·0059 respectively; and $K_3\times10^4=0{\cdot}278$ and 0·98 respectively. It is hence calculated that for 0·01*M*-$CrCl_3$ with the addition of $x$ mols of 0·1275*N*-NaOH, the soln. contains the following proportions of the hydroxychlorides:

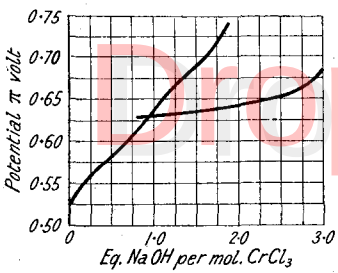


FIG. 77.—Electrometric Titration of Solutions of Chromic Chloride with Sodium Hydroxide.

| $x$ | 0 | 0·215 | 0·553 | 1·00 | 1·51 | 2·19 | 2·96 |
|---|---|---|---|---|---|---|---|
| $CrCl_3$ | 92·5 | 75·2 | 42·9 | 9·8 | 6·6 | 2·4 | 0 |
| $Cr(OH)Cl_2$ | 7·5 | 22·9 | 52·3 | 74·9 | 57·3 | 29·2 | 1·2 |
| $Cr(OH)_2Cl$ | 0 | 0·1 | 0·6 | 5·5 | 4·8 | 3·5 | 0·7 |
| $Cr(OH)_3$ | 0 | 0 | 0 | 2·4 | 20·5 | 50·0 | 78·9 |

It is also possible to calculate for the thermal values of these products $Cr(OH)Cl_2+HCl_{aq.}=CrCl_{3aq.}+H_2O+9600$ cals.; $Cr(OH)_2Cl+HCl_{aq.}=Cr(OH)Cl_2+H_2O+8060$ cals.; and $Cr(OH)_3+2HCl_{aq.}=Cr(OH)Cl_2+2H_2O+11{,}600$ cals. From the first and third equation, $Cr(OH)_3+3HCl_{aq.}=CrCl_{3aq.}+3H_2O+21{,}200$ cals., when A. Recoura

found 20,700 cals. N. Bjerrum also added that it is probable that some polymerized basic chlorides exist. Observations on the electrometric titration of the chromic chlorides were also made by J. Sand and F. Grammling, who inferred from the potential of a hydrogen electrode, and the rate of liberation of iodine from an iodide-iodate mixture that the hydrolysis of the blue salt involves the breaking down of a doubled molecule: $Cr_2(H_2O)_{12}^{\cdots\cdots}+2H_2O \rightleftharpoons 2Cr(H_2O)_6OH^{\cdot\cdot}+2H^{\cdot}$, but N. Bjerrum did not agree. H. G. Denham obtained a value for the hydrolysis constant of the blue salt twice as great as N. Bjerrum. H. T. S. Britton found that with 0·0133*N*-soln. 1·62 per cent. of the violet, and 16·4 per cent. of the green salt was hydrolyzed at 18°. A. B. Lamb and G. R. Fonda calculated the hydrolysis constant of the green salt from conductivity data to be $1·8\times10^{-6}$, and from the kinetics of the transformation $2·0\times10^{-6}$. The hydrolysis constant for the violet salt calculated from the change of conductivity with conc. is $1·52\times10^{-4}$; from the rate of transformation of the green salt, $1·65\times10^{-4}$; from the rate of inversion of cane-sugar, $1·60\times10^{-4}$; from the conductivity with or without the addition of hydrochloric acid, $1·47\times10^{-4}$, and with the addition of sodium acetate, $1·68\times10^{-4}$—mean value $1·58\times10^{-4}$.

A number of basic chlorides have been reported by A. J. Béchamp and others, but their chemical individuality has not been established. A. Moberg, for example, said that $Cr_2O_3.8CrCl_3.24H_2O$ is formed by heating hydrated chromic chloride to 120°; H. Schiff regarded it as *chromic hydroxypentachloride*, $Cr_3Cl_5(OH).4H_2O$. By heating the hydrated salt to 150°, A. Moberg obtained $Cr_2O_3.4CrCl_3.9H_2O$, which H. Schiff regarded as *chromic dihydroxytetrachloride*, $Cr_2Cl_4(OH)_2.2H_2O$, or *chromium oxytetrachloride*, $Cr_2O.Cl_4.3H_2O$; E. M. Péligot obtained the same salt by heating the hydrated chloride to 200°, digesting the product with water, and drying it at 200°. H. Löwel obtained a similar product. B. Cabrera and S. P. de Rubies obtained the salt in green and violet modifications and studied their magnetic properties. V. Kletzinsky said that *chromic oxydichloride*, $Cr_4(OCl_2)_3$, is formed by evaporating to dryness a soln. of potassium chlorochromate in conc. hydrochloric acid. A. Moberg obtained *chromic oxychloride*, $Cr_2O_3.CrCl_3$, or CrOCl, by heating the hydrated chloride to dull redness. H. Schiff obtained the hydrate, $Cr_2O_3.CrCl_3.3H_2O$, or $CrCl(OH)_2$, *chromic dihydroxychloride*, by evaporating a soln. of chromic hydroxide in chromic chloride; and E. M. Péligot obtained a similar product from a mixture of a soln. of chromic chloride and alkali hydroxide. J. M. Ordway treated 6 mols of chromic hydroxide with 2 mols of hydrochloric acid and obtained $5Cr_2O_3.2CrCl_3$, which H. Schiff regarded as *chromic heptahydroxychloride*, $Cr_2(OH)_5Cl$. It was also obtained from a mixture of ammonia and a soln. of chromic chloride. A. Besson and L. Fournier heated a mixture of chromium trioxide and silicon hydrotrichloride in a sealed tube at 100°, and obtained a brown mass of *chromium oxyheptachloride*, $Cr_2OCl_7$. There are also N. Bjerrum's *chromic hydroxypentaquodichloride*, $[Cr(H_2O)_5(OH)]Cl_2$, and his *chromic dihydroxytetraquochloride*, $[Cr(H_2O)_4(OH)_2]Cl$, previously discussed.

R. F. Weinland and W. Friedrich[2] obtained what they called *pyridinium tetrachlorohydroxychromate*, $C_5H_5N.CrCl_4.OH,H_2O$, by the action of conc. hydrochloric acid and pyridine on chromic acid. The salt forms reddish-brown leaflets or orange-yellow, hexagonal plates. The analogous *quinolinium* compound was prepared. The interesting feature about these salts is that the chromium behaves as if it were quinquevalent, and the parent oxychloride is **chromium oxytetrachloride,** $CrOCl_3$. By saturating glacial acetic acid with hydrogen chloride, adding chromium trioxide, and then a soln. of alkali chloride in acetic acid soln., R. F. Weinland and M. Fiederer obtained **potassium chromium oxypentachloride,** $CrOCl_3.2KCl$, in dark garnet-red, rhombic prisms. The oxidizing power of the salt gradually diminishes when it is kept in a desiccator. The corresponding **rubidium chromium oxypentachloride,** $CrOCl_3.2RbCl$; **cæsium chromium oxypentachloride,** $CrOCl_3.2NH_4Cl$, are similarly prepared. The crystalline forms are similar to those of the corresponding salts of columbium and molybdenum. The cæsium salt is isomorphous with $CrOCl_3.2CsCl$. It was supposed that these products are salts of quinquevalent chromium, and a similar remark applies to various analogous compounds prepared by F. Olsson—*e.g.* $N(CH_3)_4CrOCl_4$; $N(C_2H_2)CrOCl_4$; etc.

J. J. Berzelius[3] discovered **chromium dioxydichloride,** or **chromyl chloride,** $CrO_2Cl_2$, which he obtained by distillation from a mixture of a chromate, sodium

chloride, and conc. sulphuric acid. He thought that it was a higher chloride of chromium, but H. Rose proved that it contained oxygen. It was also analyzed by T. Thomson, P. Walter, and T. E. Thorpe, and these results, as well as the vap. density determinations of J. B. A. Dumas, P. Walter, E. Moles and L. Gomez, and E. Carstenjen; the f.p. determinations—*vide infra*—of R. E. Meyer and H. Best, and E. Moles and L. Gomez; and the b.p. determinations of E. Moles and L. Gomez, and G. Oddo and E. Serra are in agreement with the formula just indicated. The chromium is assumed to be sexivalent. E. R. Darling compiled a bibliography on the chemistry of chromyl chloride. G. Mazzaron said that the chlorides of silver, mercury, gold, and platinum, and antimony oxychloride give chlorine, not chromyl chloride when treated with potassium dichromate and sulphuric acid. F. Wöhler, A. Vogel, P. Walter, H. Rose, E. Burcker, E. Moles and L. Gomez, and G. Errera used modifications of this process: $3K_2CrO_4+6NaCl+12H_2SO_4=6KHSO_4+6NaHSO_4+3CrO_2Cl_2+6H_2O$. J. B. A. Dumas used lead chromate; potassium dichromate was used by T. Thomson. T. Thomson said that a better yield is obtained by using fuming sulphuric acid: $K_2Cr_2O_7+4NaCl+3H_2S_2O_7=2CrO_2Cl_2+K_2SO_4+2Na_2SO_4+3H_2SO_4$—but, added A. Étard, if the fuming acid be in excess, the chromyl chloride suffers some decomposition: $6CrO_2Cl_2+3H_2S_2O_7=2Cr_2(SO_4)_3+2CrO_3+6Cl_2+3H_2O$. H. Rose, and J. B. A. Dumas said that so much chlorine may be evolved that if the receiver is very cold, the product may solidify. P. Walter, and E. Carstanjen purified the liquid by fractional distillation for a number of times whereby the chlorine is given off first, and then the chromyl chloride, while sulphuric acid remains in the retort. T. E. Thorpe purified the liquid by fractional distillation in a current of carbon dioxide; and E. Moles and L. Gomez repeatedly fractioned the product after agitation with mercury. According to the Permutit A. G., an acid chloride, like chlorosulphonic acid, reacts with chromic acid or a chromate in the presence of conc. sulphuric acid or other diluting agent which does not decompose chromyl chloride; the acid anhydride—sulphur trioxide when chlorosulphonic acid is used—is converted into an acid chloride by the introduction of hydrochloric acid, and then acts on fresh chromic acid.

K. Heumann and P. Köchlin, and H. Moissan obtained chromyl chloride by the action of hydrogen chloride on dry chromium trioxide. W. Autenrieth treated chromium trioxide with 35 to 40 per cent. hydrochloric acid, and obtained a 35 per cent. yield of chromyl chloride, the yield is reduced with more dilute acid until with 20 per cent. hydrogen chloride, only chlorine is given off. H. Moissan also replaced the chromium trioxide with alkali or alkaline earth chromates; and moist chlorine can be used in place of hydrogen chloride at a temp. of 150°. L. Henry passed hydrogen chloride into sulphuric acid with chromium trioxide in suspension; and R. J. Meyer and H. Best suspended the chromium trioxide in glacial acetic acid; while H. D. Law and F. M. Perkin heated a soln. of chromium trioxide, conc. sulphuric acid, and conc. hydrochloric acid. A. Geuther chlorinated the chromium trioxide by heating it with anhydrous ferric or chromic chloride: $2FeCl_3+3CrO_3=Fe_2O_3+3CrO_2Cl_2$; H. Schiff, by phosphorus pentachloride; H. Erdmann, by chloroform: $2CHCl_3+CrO_3+O_2=2COCl_2+H_2O+CrO_2Cl_2$; A. Michael and A. Murphy, by carbon tetrachloride in a sealed tube at 150°–175°; and H. S. Fry, by acetyl chloride on a soln. of chromium trioxide in chloroform and acetic acid. A. Rosenstiehl treated chromates with pyrosulphuryl chloride; and K. Heumann and P. Köchlin used chlorosulphonic acid. E. M. Péligot treated potassium chlorochromate with sulphuric acid. H. Moissan found that moist chlorine attacks uncalcined chromic oxide at 440°, forming first chromic chloride which then reacts with the moisture forming chromyl chloride, and hydrogen chloride. The reaction is reversed at a higher temp. At 440°, also, oxygen acts on chromic chloride, forming chromyl chloride. P. Pascal found that chromyl chloride is formed by slowly heating pentachromyl hexachloride. F. G. Nunez prepared chromyl chloride of a high degree of purity for at. wt. determinations.

T. Thomson described chromyl chloride as a blood-red liquid which appears

black by reflected light. G. J. Stoney and J. E. Reynolds found that chromyl chloride forms a yellowish-red vapour resembling nitrogen peroxide and E. Moles and L. Gomez observed that it freezes to form pale red, acicular crystals. T. Thomson gave 1·913 for the **specific gravity** of the liquid at 10°; P. Walter, 1·91 at 21°; T. E. Thorpe, 1·961 at 0°; 1·92 at 25°; and 1·7578 at the b.p. 115·9°; and E. Moles and L. Gomez, 2·0515 to 2·0528 at —47°/4°; 1·9582 to 1·9591 at 0°/4°; and 1·9113 to 1·9124 at 25°/4°. J. B. A. Dumas found the **vapour density** (air unity) to be 5·35 at 127° and 5·69 at 147°—when the theoretical value for $CrO_2Cl_2$ is 5·35; P. Walter found 5·9 at 143·7°; E. Carstanjen, 5·39 at 200°: and E. Moles and L. Gomez, 5·31 at 181°. Hence the vapour is not dissociated at these temp. T. E. Thorpe gave for the **thermal expansion** of unit vol. at 0° to $v$ vols. at $\theta°$, $v=1+0{\cdot}0_395860\theta+0{\cdot}0_51073\theta^2+0{\cdot}0_81962\theta^3$. R. J. Meyer and H. Best found that the mol. wt., calculated from **the depression in the freezing point** of acetic acid, is 208 to 218—the theoretical value for $CrO_2Cl_2$ is 155. This shows that polymerization is taking place. E. Moles and L. Gomez found 175 to 189 with this solvent; 153 to 161 with phosphoryl chloride; 175·5 to 241 with nitrobenzene; 185 to 399 with ethylene dibromide; 91·8 to 97·8 with stannic bromide; and 193 to 215 with antimony pentachloride. Dil. soln. in nitrobenzene and ethylene dibromide show ionization, passing, with increasing concentration, into association. G. Oddo and A. Casalino found for 0·9694 and 2·4708 grms. of chromyl chloride in 100 grms. of the complex $SO_3.2POCl_3$ respectively 188 and 237 for the mol. wt.—theoretical 155. G. Oddo and E. Serra found from **the raising of the boiling point** of soln. in benzene, and carbon tetrachloride, mol. wts. between those required for the single and for the double molecule. E. Moles and L. Gomez obtained normal values when the results are corrected for the volatility of the solute—166·7 to 170·6 was obtained with carbon tetrachloride, and 164 to 172 with carbon disulphide. E. Beckmann gave 55·0 for the **ebulliscopic constant**—the mol. rise of the b.p.—of chromyl chloride when it is used as a solvent for mol. wt. determinations. E. Moles and L. Gomez gave —96·5° for the **melting point**; and for the **boiling point** P. Walter gave 118°; E. Carstanjen, 117·6° at 753 mm.; H. D. Law and F. M. Perkin, 118·5°–116°; T. E. Thorpe, 115·9° at 733 mm. and 116·8° at 760 mm.; and E. Moles and L. Gomez, 116·3° at 760 mm. The b.p., $\theta°$, at different press., $p$ mm., are:

| $p$ . . | 232·3 | 338·0 | 424·0 | 525·0 | 645·8 | 750·8 | 763·1 | 839·1 |
|---|---|---|---|---|---|---|---|---|
| B.p. . | 79·4° | 90·5° | 97·4° | 104·5° | 111·0° | 116·3 | 117·0° | 120·4° |

The data can be represented by $\theta=53{\cdot}63+0{\cdot}1271p-0{\cdot}000058p^2$. M. Berthelot found that the mol. **heat of soln.** in 100 parts of water at 8° is 16·67 Cals. The **absorption spectrum** of chromyl chloride was first examined by W. H. Miller, H. Mayer, B. Käbitz, R. Ritschl, and A. C. S. van Heel. G. J. Stoney and J. E. Reynolds found that the absorption spectrum shows orange yellow and green lines; they also observed that, excepting a small strip in the red, the vapour absorbs all the spectrum of a colourless flame. M. R. Read said that chromyl chloride imparts a pale white light to the colourless gas-flame; and F. Gottschalk and E. Drechsel added that if the vapour mixed with oxygen be passed into a non-luminous gas-flame, the colour is a paler violet than that imparted to the flame by potassium, and the flame spectrum shows three violet, eight green, one yellow, three orange-red, and two red lines. A. Cornu could not find any regularities in the spectral lines. According to B. Käbitz, liquid chromyl chloride absorbs the whole visible spectrum.

J. W. Hittorf, and E. Moles and L. Gomez found chromyl chloride to be a non-conductor of electricity. E. Moles and L. Gomez found that the mol. **electrical conductivity** is 5·05, 2·60, 1·38, and 0·96 mhos with soln. containing respectively 0·0323, 0·0724, 0·1398, and 0·2170 mol of $CrO_2Cl_2$ per litre of dried nitrobenzene at 25°. If the solvent is not thoroughly dried, the conductivity is two to five times as great, and it increases with time. The mol. conductivity decreases with increasing concentration, and the curves are parallel with those for the mol. wt. of chromyl

chloride in the same solvent. P. Walden found the **dielectric constant** of the liquid to be 2·6 at 20°.

A. Étard said that chromyl chloride is very stable if it be protected from **light,** but in light it decomposes slowly forming chlorine and an oxide or oxychloride of chromium. F. Wöhler, and H. Quantin found that chromyl chloride is decomposed by **heat,** for when passed through a red-hot tube it furnishes crystals of chromic oxide: $2CrO_2Cl_2=Cr_2O_3+O+2Cl_2$; F. Wöhler, that a little above 300° it forms magnetic chromic chromate; and T. E. Thorpe, that at 180° to 190°, in a sealed tube, it forms chlorine and trichromyl chloride. If the vapour of chromyl chloride, mixed with dry **hydrogen,** be passed through a red-hot tube, A. Schafarik observed that it decomposes: $3CrO_2Cl_2+3H_2=6HCl+Cr_2O_3.CrO_3$; and when heated for a longer time, chromic oxide and oxygen are formed. F. Gottschalk and E. Drechsel said that a colourless gas-flame charged with a mixture of hydrogen and chromyl chloride becomes luminous, and deposits chromic oxide on a cold surface placed in the flame. J. B. A. Dumas, and P. Walter found that **water** decomposes chromyl chloride with the development of much heat forming a mixture of chromic and hydrochloric acids. J. J. Berzelius called the liquid *chlorwasserstoffsaure Chromsäure,* apparently regarding it as a special compound, for it was said to be formed by the action of hydrochloric acid on lead or silver chromate at the ordinary temp. The liquid is said to dissolve gold, and H. Moser found that when warmed chlorine is evolved. A. Étard, and J. B. A. Dumas observed that chromyl chloride absorbs **chlorine** freely, and becomes almost solid; H. W. B. Roozeboom found that the proportion of chlorine absorbed is dependent on the press. and temp. It increases rapidly as the temp. falls to −26° so that at 760 mm. press., a sat. soln. contains at 0°, 0·70 gram-atoms; at −14°, 1·24; at −21°, 2·31; and at −26°, 3·00. At 0°, the press., $p$ mm., of soln. with $N$-gram-atoms of chlorine is:

| | | | | | | |
|---|---|---|---|---|---|---|
| Cl | 1·70 | 1·40 | 1·30 | 1·20 | 1·04 | 0·91 |
| $p$ | 1302 | 1198 | 1150 | 1101 | 1016 | 923 mm. |

DropBooks

P. Walter said that chromyl chloride dissolves **iodine** without being decomposed; and R. W. E. McIvor said that when the mixture is distilled, iodine monochloride and trichromyl chloride are formed. H. Quantin found that dry **hydrogen chloride** reacts with chromyl chloride at a red-heat forming water, chlorine, and chromic oxide. J. B. A. Dumas found that **sulphur** decomposes chromyl chloride with a hissing noise; K. T. Kemp, and W. Gregory observed that a rose-coloured powder separates possibly chromic chloride; and T. Thomson added that when flowers of sulphur is moistened with it, the mixture ignites and burns with a red flame. K. T. Kemp found that if **hydrogen sulphide** be passed into chromyl chloride, the vessel becomes hot, hydrogen chloride is evolved, and a green powder is formed which A. Vogel said is probably chromic oxide. K. T. Kemp also found that if chromyl chloride vapour be passed through a narrow jet into the vapour of **sulphur monochloride,** vivid combustion occurs, and a rose-coloured powder is formed. K. Heumann and P. Köchlin observed that **chlorosulphonic acid** decomposes chromyl chloride; and, as indicated above, a similar remark applies to **pyrosulphuric acid.**

According to T. Thomson, chromyl chloride in **ammonia** solidifies with brilliant incandescence to form a dark brown mass, and with a more prolonged action on the residue, A. Schrötter, and C. E. Ufer found that chromium nitride or a mixture of nitride and oxide is formed. J. Heintze observed that with ammonia largely diluted by air, the residue, after washing, consists of chromic oxide. S. Rideal represented the reaction with dry ammonia, $3CrO_2Cl_2+8NH_3=6NH_4Cl+N_2+Cr_2O_3.CrO_3$. V. Thomas found that with **nitric oxide** and chromyl chloride vapour, a brown mass of **chromic dinitroxylheptoxypentachloride,** $Cr_5Cl_5O_7.2NO_2$, is formed; P. Pascal prepared pentitahexachloride by the action of nitric oxide—*vide infra.* J. B. A. Dumas, and P. Walter found that chromyl chloride explodes with **phosphorus,** and light is emitted at the same time—the effect is produced by

a drop of the liquid and a piece of phosphorus the size of a pin's head. T. Thomson said that the phosphorus must be moistened to produce the explosion; when dry it is without action, and the flame of phosphorus is extinguished in the vapour of chromyl chloride. A. Michaelis observed that each drop of chromyl chloride added to well-cooled **phosphorus trichloride** produces a hissing noise, incandescence, and sometimes an explosion: $4CrO_2Cl_2+6PCl_3=4CrCl_3+3POCl_3+PCl_5+P_2O_5$. H. Schiff represented the reaction with **phosphorus pentachloride**: $2CrO_2Cl_2+4PCl_5=4POCl_3+3Cl_2+2CrCl_3$, and R. Weber, and A. W. Cronander added that some **chromium phosphoctochloride,** $CrCl_3.PCl_5$, is formed. H. S. Fry and J. L. Donnelly obtained the complex chromyl phosphoheptachloride, $CrO_2Cl_2.PCl_5$, by the action of chromyl chloride on a dry carbon tetrachloride soln. of phosphorus pentachloride. W. T. Casselmann showed that **phosphoryl chloride** reacts in the cold with chromyl chloride forming a black substance which decomposes at 100° as symbolized by $10POCl_3+12CrO_2Cl_2=18Cl_2+5P_2O_5+3Cr_2O_3+6CrCl_3$. E. Moles and L. Gomez found that chromyl chloride is soluble in phosphoryl chloride. H. S. Fry and J. L. Donnelly found that in soln. of dry carbon tetrachloride phosphorus trichloride reacts: $2CrO_2Cl_2+3PCl_3=PCl_5+2CrOCl.POCl_3$, and the deliquescent **chromium trioxyphosphotetrachloride** reacts with water: $CrOCl.POCl_3+2H_2O=CrCl_3+HCl+H_3PO_4$. On ignition, the complex **chromium trioxytrichloride,** CrOCl, or $Cr_2O_3.CrCl_3$ is formed. With **phosphorus tribromide, chromium trioxyphosphodichlorotribromide,** $2CrOCl.POBr_3$, is formed: $2CrO_2Cl_2+3PBr_3=2CrOCl.POBr_3+PBr_3Cl_2$. With **phosphorus pentabromide,** the complex **chromyl phosphodichloropentabromide,** $CrO_2Cl_2.PBr_5$, and **chromium dioxyphosphochlorotribromide,** $CrOCl.POBr_3$, are produced; with **phosphorus triiodide,** the complex **chromyl phosphodichlorotriiodide,** $CrO_2Cl_2.PI_3$, is formed, and it is decomposed by water: $2(CrO_2Cl_2.PI_3)+4H_2O=4HCl+4HI+I_2+2CrPO_4$; and with **phosphorus diodide,** the complex **chromyl phosphodichloridiiodide,** $CrO_2Cl_2.PI_2$ is formed: E. Moles and L. Gomez found that chromyl chloride is soluble in **antimony pentachloride,** and in **stannic bromide.**

J. B. A. Dumas, and T. Thomson found that **carbon** has no action on chromyl chloride. J. R. Mourelo and A. G. Banus found that the dried vapour of chromyl chloride mixed with air does not react: $4CrO_2Cl_2+4C+O_2=2Cr_2O_3+4COCl_2$, but chromic oxide is formed in the hot part of the tube and chromic chloride is deposited in the cooler part. It is difficult to get the charcoal free from hydrocarbons. The reaction of a mixture of chlorine and chromyl chloride with red-hot carbon is symbolized: $2CrO_2Cl_2+Cl_2+4C=2CrCl_3+4CO$. Chromyl chloride in general acts as an oxidizing and chlorinating agent on organic compounds: and in many cases the reaction is violent or explosive. H. Quantin found that when a mixture of the vapour of **carbon monoxide** and chromyl chloride is passed through a red-hot tube, chromic oxide and chloride are formed; and if the carbon monoxide be mixed with chlorine, and the temp. be 500° to 600°, carbon dioxide and chromic chloride are formed. P. Pascal obtained chromyl pentitahexachloride by reduction with carbon monoxide—*vide infra*. H. Erdmann, A. Emmerling and B. von Lengyel, and H. Quantin symbolized the reaction with **carbon tetrachloride**: $2CrO_2Cl_2+4CCl_4=2CrCl_3+4COCl_2+3Cl_2$. At ordinary temp. G. Oddo and E. Serra, and E. Moles and L. Gomez found it to be soluble in carbon tetrachloride; and R. J. Meyer and H. Best added that there is no action with carbon tetrachloride; and J. B. A. Dumas, none with **carbon disulphide,** and E. Moles and L. Gomez found that chromyl chloride dissolves in this liquid; and A. Étard found that in a sealed tube carbon disulphide reacts forming a complex mixture of products; and under similar conditions chloroform, with chromic acid and oxygen, furnishes carbonyl chloride, hydrogen chloride, and chromyl chloride; H. Erdmann, and A. Emmerling and B. von Lengyel represented the reaction: $2CHCl_3+CrO_3+O_2=2COCl_2+CrO_2Cl_2+H_2O$. F. Wöhler, and K. T. Kemp found that **ethylene** reacts forming ethylene chloride. E. Moles and L. Gomez found that it is soluble in **ethylene dibromide,** and in **nitrobenzene.** T. Thomson said that **turpentine** is

inflamed by chromyl chloride, while **wood-spirit, camphor,** and **olive oil** are decomposed; F. Wöhler found that **indigo** is not acted upon. F. Wöhler, P. Walter, and T. Thomson observed that with absolute **alcohol,** enough heat is generally evolved to produce combustion, and may be an explosion with violent projection of the liquids. R. J. Meyer and H. Best found that alcohol, **ether,** and **acetone** react with incandescence; **benzene** is slowly attacked, but **toluene,** *o*-**xylene, pyridine,** and **quinoline** are vigorously attacked. A. Étard studied the reaction with **acetic acid** in a sealed tube at 100°, and obtained $Cr_2O_7\{Cr_2(C_2H_3O_2)_5\}_2.8H_2O$. E. Moles and L. Gomez studied soln. in acetic acid. The **aliphatic hydrocarbons,** $R.CH_3$, form the corresponding aldehyde, R.CO.H, with the formation of the intermediate compounds:

$$R.CH\begin{matrix}O.Cr(OH)Cl_2\\O.Cr(OH)Cl_2\end{matrix}\rightarrow R.CH\begin{matrix}O.CrO.Cl\\O.CrO.Cl\end{matrix}\rightarrow R.CO.H$$

The reactions with aliphatic hydrocarbons, and various other organic compounds were studied by A. Étard, V. von Richter, P. Friedländer, E. Carstanjen, G. G. Henderson and co-workers, A. Haller, J. Bredt and W. Jagelki, D. Spence and J. C. Galletly, etc. Many of these reactions are discussed by G. Rohde, *Das Chromylchlorid und die Étard'sche Reaktion* (Stuttgart, 1901). J. B. A. Dumas, and P. Walter found that **mercury** is violently attacked by chromyl chloride.

According to E. Zettnow,[4] when chromyl chloride is distilled from a mixture of potassium chlorochromate and sulphuric acid, there is also formed a brown mass which is separated from the chromyl chloride, dissolved in water, and dried. Its composition corresponds with **chromyl tritadichloride,** $(CrO_2)_3Cl_2$. R. J. Meyer and H. Best represented it by the formula $Cl.CrO.O.CrO_2.O.CrO.Cl$. T. E. Thorpe made it by heating chromyl chloride in a sealed tube at 180° to 190°: $3CrO_2Cl_2=Cr_3O_6Cl_2+2Cl_2$; and R. W. E. McIvor, by distilling the iodine monochloride from a soln. of iodine in chromyl chloride: $3CrO_2Cl_2+2I_2=4ICl+Cr_2O_2Cl_2$. P. Pascal made it by heating chromyl pentitahexachloride. The black amorphous compound, said T. E. Thorpe, is reduced to chromic oxide when heated to a low temp. in hydrogen; and R. W. E. McIvor obtained chromic oxide by heating it in air. According to T. E. Thorpe, and R. W. E. McIvor, when exposed to air the tritadichloride deliquesces to a reddish-brown syrup which smells of chlorine; it is freely soluble in water forming a dark brown liquid which gives off chlorine; a nitric acid soln. behaves as if it contained hypochlorous acid; with hydrochloric acid, it forms a dark brown soln. which, when heated, gives off chlorine and forms chromic chloride; with ammonia it forms ammonium chloride and chromate, and chromic chromate; and, according to S. G. Rawson, it is scarcely soluble in carbon disulphide, but forms red soln. with alcohol, and ether.

According to P. Pascal, **chromyl pentitahexachloride,** $(CrO_2)_5Cl_6$, is formed when nitric oxide is passed into chromyl chloride, cooled in a bath of water; heat is evolved and a crystalline paste is formed, nitrosyl chloride is evolved: $5CrO_2Cl_2+4NO=4NOCl+(CrO_2)_5Cl_6$, when the excess of chromyl chloride is removed, in vacuo at 100°, there remains the pentitahexachloride as a brown crystalline powder of sp. gr. 2·51. Carbon monoxide in sunlight can effect the same reduction as nitric oxide. Unlike chromyl chloride, the pentitahexachloride is strongly magnetic so that the function of chromium in the chromyl, $CrO_2$-radicle, and in the $(CrO_2)_5$-radicle appears to be different. In fact, chlorine, which acts only above 150°, slowly converts the pentitahexachloride back to chromyl chloride. Chromyl pentitahexachloride is deliquescent, and readily dissolves in water to a dark brown soln. with an odour of chlorine and the reactions of chromium salts, chromic acid, and hydrochloric acid. If slowly heated to 150°, chromyl chloride is evolved, and if quickly heated, chlorine only, the solid product in both cases being the tritadichloride, $(CrO_2)_3Cl_2$. Above 180° oxygen is evolved, leaving an insoluble brownish-black residue of $Cr_6O_9Cl_4$. Towards hydrogen, hydrogen sulphide, etc., chromyl subchloride acts as a chlorinating agent at low temp., whilst above 200° its action is

generally an oxidizing as well as a chlorinating one. Moist gaseous ammonia acts very violently, the products being ammonium chloride, oxygen, and the oxides $CrO_2$ and $Cr_2O_3$. Generally speaking, however, chromyl pentitahexachloride is less reactive than chromyl chloride. When chromyl pentitahexachloride is suspended in dry ether, and a current of slightly moist ammonia is passed through, nitrogen is evolved, and ammonium chloride and a brown, amorphous precipitate remain. Ammonium chromate and chromium chromate are removed from the precipitate by washing, and the pale brown, insoluble residue when dried at 90° has the composition of an explosive *ammonium chromite*, $(NH_4O)_6(CrO_2)_5$.

According to G. Herfeldt,[5] if eq. proportions of chromium trioxide and chromyl chloride are heated in a sealed tube at 180°, impure **chlorochromic oxide,** $Cr_2O_5Cl_2$, or $(CrO_2Cl)_2O$, is formed. It is suggested that it is the anhydride, $CrO_2Cl–O–CrO_2Cl$, of the hypothetical *chlorochromic acid*, $HCrO_3Cl$, or $HO.CrO_2Cl$. The pale red compound is said to be very reactive, for it reacts explosively with alcohol, pyridine, and quinoline. A number of salts, **chlorochromates,** has been prepared. E. M. Péligot, and S. Löwenthal prepared **ammonium chlorochromate,** $(NH_4)CrO_3Cl$, as in the case of the potassium salt. It has the same appearance, but is much more soluble. S. Löwenthal prepared **lithium chlorochromate,** $LiCrO_3Cl$, from an aq. soln. of chromyl chloride and lithium chromate mixed with acetic acid. The yellowish-red crystals are, according to A. Fock, monoclinic ; they are easily fused to a reddish-brown liquid ; and are freely soluble in water. E. M. Péligot obtained **sodium chlorochromate,** $NaCrO_3Cl.2H_2O$, by adding sodium chloride to a conc. aq. soln. of chromyl chloride ; G. Prätorius, by adding chromyl chloride to a conc. soln. of sodium carbonate in chromic acid, and allowing the mixture to stand some days in a desiccator over conc. sulphuric acid ; and A. Ditte, by adding sodium chloride to a soln. of chromic acid. The dark reddish-yellow, prismatic crystals, when dried by press. between porous tiles lose water, and form an amorphous, yellow mass. If kept in a badly closed vessel, water of crystallization is taken up again. The compound melts by the heat of the hand, and at 110° loses chlorine, and water.

E. M. Péligot obtained **potassium chlorochromate,** $KCrO_3Cl$, by boiling potassium dichromate for a short time with an excess of hydrochloric acid, and cooling the liquid : $K_2Cr_2O_7+2HCl=H_2O+2KCrO_3Cl$—if boiled for too long a time some chromic acid is reduced ; he also obtained it by mixing equimolar parts of potassium chloride and chromic acid in aq. soln., and adding hydrochloric acid—G. Herfeldt used a similar process. E. M. Péligot, and A. Werner, treated chromyl chloride with a sat. soln. of potassium chloride : $CrO_2Cl_2+KCl+H_2O=2HCl+KCrO_3Cl$ ; A. Ditte added potassium chloride to a hot soln. of an eq. quantity of chromic acid ; A. Michaelis, by the action of phosphorus trichloride on potassium dichromate ; A. Geuther added chromyl chloride to soln. of potassium chromate in dil. acetic acid : $K_2CrO_4+CrCl_2O_2=2KCrO_3Cl$ ; and also violet chromic chloride to molten potassium dichromate, $3K_2Cr_2O_7+2CrCl_3=Cr_2O_3+6KCrO_3Cl$. If the temp. is too high, chlorine may be given off. If the cold mass be dissolved in water acidified with acetic acid, and evaporated, the excess of potassium dichromate first separates out, and then follows the potassium chlorochromate. L. Varenne discussed the constitution of these salts, which are usually represented $RO.CrO_2.Cl$, or according to A. Werner's scheme :

$$\left[\begin{matrix} O \\ OCrCl \\ O \end{matrix}\right]R$$

E. M. Péligot said that the salt forms rectangular prisms, the colour of potassium dichromate ; and that the salt is stable in air ; A. Ditte found that the salt furnishes yellow needles which darken in air ; and R. J. Meyer and H. Best, that when crystallized from acetic acid soln. over sulphuric acid, the salt is stable. G. N. Wyrouboff gave for the axial ratios of the monoclinic prisms $a:b:c=0{\cdot}9653:1:1{\cdot}0174$, and $\beta=90°\ 20'$. L. Playfair and J. P. Joule gave 2·49702 for

the sp. gr. at 39°. J. Heintze, and J. G. Gentele said that when heated to 100°, the salt gives off chlorine; G. Herfeldt observed no evolution of chlorine below 250°, and he said that even after heating at 500° to 600° for some hours about 8 per cent. of chlorine remains in the residue. A. Streng also found that some oxygen is given off. A. Schafarik found that the salt readily fuses to a dark brown liquid with the evolution of chlorine and the formation of chromic oxide. A. C. Oudemans represented the reaction: $4KCrO_3Cl=K_2Cr_2O_7+Cr_2O_3+2KCl+Cl_2+O_2$; and A. Ditte noticed that a little chromyl chloride is also formed. F. Morges made some observations on the electrolysis of soln. of the salt. A. Ditte said that the salt is not decomposed when dissolved in water; and F. Morges gave 4·65 Cals. for the heat of soln. in 488 mols of water. E. M. Péligot found that the evaporation of the aq. soln. of the salt gives potassium dichromate; but with dil. hydrochloric acid the salt does not decompose; with conc. hydrochloric acid, potassium chloride, chromic chloride, and chlorine are formed. A. Ditte also noticed the evolution of chlorine when the salt is treated with hydrochloric acid. V. Kletzinsky observed that a violet mixture of potassium chloride and basic chromic chloride, $Cr_2O_3.2CrCl_3$—or possibly potassium chromium chloride, $KCrCl_4$—is formed by evaporating the soln. in conc. hydrochloric acid. E. M. Péligot found that with conc. sulphuric acid, chromyl chloride is evolved. H. Schiff gave for the reaction with fused potassium sulphate: $K_2SO_4+KCrO_3Cl=KCl+KO.SO_2.O.CrO_2.OK$; and with potassium hydrosulphate; $KHSO_4+KCrO_3Cl=HCl+KO.SO_2.O.CrO_2.OK$. J. Heintze observed that with ammonia, ammonium chloride, potassium chromochromate, etc., are formed, while A. Leist said that the products are potassium and ammonium dichromates, ammonium chloride, and chromic oxide. If the salt under ether, freed from moisture and alcohol, be treated with dry ammonia, chromium amidochromate is formed. A. Naumann found the salt to be soluble in acetone. J. Heintze said that the salt does not act on ether or benzene, but it oxidizes alcohol, and aniline; and a hot conc. soln. of potassium cyanide forms cyanogen chloride and potassium chromate.

E. M. Péligot reported **calcium chlorochromate,** $Ca(CrO_3Cl)_2.5H_2O$, to be formed as in the case of the potassium salt; but G. Prätorius could obtain it only by mixing 10 grms. of calcium carbonate or acetate with the theoretical quantity of solid chromium trioxide, forming 30 c.c. of acetic acid—containing an equal part of water and chromic acid—over the mixture and adding the calculated quantity of chromyl chloride. The reddish-yellow liquid is warmed on a water-bath, and the salt crystallizes out on cooling. The yellow, deliquescent salt melts in its water of crystallization at 56°. G. Prätorius obtained **strontium chlorochromate,** $Sr(CrO_3Cl)_2.4H_2O$, from an acetic acid soln. of strontium chromate, chromium trioxide and chromyl chloride. The carmine-red crystals melt without decomposition at 72°; they lose water when confined over sulphuric acid; and they form an orange liquid with water. Only impure, orange-yellow crystals of **barium chlorochromate** were prepared by G. Prätorius from glacial acetic acid soln. of barium chromate and chromyl chloride; but he obtained from the soln. a complex with acetic acid, **barium tetracetochlorochromate,** $Ba(CrO_3Cl)_2.4CH_3COOH.2H_2O$. He also obtained yellow crystals of **barium chlorochromatochloride,** $Ba(CrO_3Cl)Cl$, probably rhombic, from the mother-liquor remaining after the separation of the preceding salt, treated with conc. acetic acid on a water-bath. The hygroscopic crystals are freely soluble in water, and the yellow soln. when warmed deposits barium chromate; when the salt is heated, chromyl chloride is evolved. If the mother-liquor just indicated be acidified with dil. hydrochloric acid, yellow, six-sided plates of the *hydrate,* $Ba(CrO_3Cl)Cl.H_2O$, are formed. E. M. Péligot, and S. Löwenthal prepared **magnesium chlorochromate,** $Mg(CrO_3Cl)_2.9H_2O$, as in the case of the potassium salt, and G. Prätorius, from a soln. of magnesium carbonate in an excess of chromic acid and dil. hydrochloric acid. The reddish-yellow, hygroscopic, rhombic crystals melt in their water of crystallization at 66°; they form the *pentahydrate* when confined over sulphuric acid; and they lose chlorine

and water at 135° to 140°. The salt is freely soluble in water. G. Prätorius prepared **zinc chlorochromate,** $Zn(CrO_3Cl)_2.9H_2O$, as in the case of the magnesium salt; and S. Löwenthal, from a cold, conc. soln. of zinc chloride and chromic acid acidified with acetic acid, and he dried the crystals on porous tiles. The reddish-yellow, hygroscopic, prismatic or tabular crystals decompose over sulphuric acid in a desiccator, giving off chlorine; they melt in their water of crystallization at 37·5°; they lose some water and chlorine at 100°. Chlorine is evolved when the salt is treated with lead oxide. M. Lachaud and C. Lepierre prepared impure **thallous chlorochromate,** $TlCrO_3Cl$, from a soln. of thallous chloride and chromic acid in a little water. The prismatic crystals are decomposed by water into thallous chloride and chromic acid. L. Bourgeois fused a mixture of lead chromate and chloride and obtained hexagonal prisms of **lead dichlorochromate,** $PbCl_2.PbCrO_4$. W. J. Sell prepared **chromic hexacarbamidochlorochromate,** $[Cr(CON_2H_4)_6](CrO_3Cl)_2.3H_2O$. G. Prätorius prepared hygroscopic, dark orange-yellow crystals of **cobalt chlorochromate,** $Co(CrO_3Cl)_2.9H_2O$, from a mixed soln. of chromic acid, cobalt carbonate and chromyl chloride. The crystals melt in their water of crystallization at 40° without decomposition; and they lose water on exposure to air. For **cobaltic hexamminochlorochromate,** $[Co(NH_3)_6]Cl(CrO_4).nH_2O$, *vide supra*, the chromates. The corresponding **nickel chlorochromate,** $Ni(CrO_3Cl)_2.9H_2O$, was obtained by G. Prätorius in a similar manner to the cobalt salt; the dark orange-yellow, hygroscopic crystals melt in their water of crystallization at 46° to 48°.

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## § 24. The Chromium Ammines

The ammines of chromium were first obtained by E. Frémy [1] in 1858, and they were soon afterwards studied by P. T. Cleve, and then by J. Morland, A. Reinecke, and S. M. Jörgensen. A. Werner showed that as in the case of the cobalt, and platinum ammines, most of the chromium ammines fitted into the system based on his co-ordination theory—**8**. 49, 19. I. I. Chernyeff studied the inner structure of the chromium ammines. Extensive investigations on the chromium ammines have been made by P. Pfeiffer and his fellow-workers, and the following summary is based on his reports :

*A.—Compounds with one chromium atom in the nucleus.*

I.—**The hexammine family,** or compounds of the tervalent basic group : $[CrA_6]'''$.

(i) *Hexammines*, $[Cr(NH_3)_6]X_3$. These salts are the so-called *chromium luteosalts*, studied by S. M. Jörgensen, A. Benrath, O. T. Christensen, W. R. Lang and C. M. Carson, J. Meyer and L. Speich, H. J. S. King, P. Pfeiffer and S. Basci, L. A. Welo, and P. Pfeiffer and M. Haimann, J. Petersen, O. Stelling, O. Hassel and G. B. Næss, E. Wilke-Dörfurt and co-workers, and A. Werner and A. Miolati. These salts include : (1) chloride and (2) its mercurichloride, and (3) chloroplatinate ; (4) bromide and (5) its bromoplatinate ; (6) iodide, and (7*a*) its sulphate,

and (7*b*) selenate; (8) perchlorate; (9) sulphate and (10) its chloroplatinate; (11) nitrate and (12) its chloroplatinate; (13) dinitratofluosulphonate; (14) phosphate and (15) its sodiopyrophosphate; (16) oxalate and (17) its chromioxalate, (18) its cobaltioxalate; (19) cyanide and (20) its chromicyanide, (21) its ferricyanide; (22) its cobalticyanide; (23) picrate; (24) dipicrylamide; (25) 2 : 4-dinitro-$\alpha$-naphthoxide; (26) 2 : 4-dinitro-$\alpha$-naphthoxide-$\gamma$-sulphonate; (27) 2 : 3 : 6-trinitrophenoxide; (28) 1 : 2-naphthaquinone-1-oximate (1-nitroso-$\beta$-naphthoxide); (29) 1 : 2-dihydroxyanthraquinone; (30) picramate, and (31) permanganate.

(ii) *Trisethylenediamines*, $[Cr\ en_3]X_3$. These salts were studied by J. Meyer and L. Speich, L. A. Welo, P. Pfeiffer, P. Pfeiffer and A. Trieschmann, P. Pfeiffer and M. Haimann, and A. G. Berghman. They include: (1) chloride; (2) bromide; (3) iodide; (4) nitrate; (5) selenate; (6) oxalate, and (7) its chromioxalate, and (8) cobaltic oxalate; (9) cyanide, and (10) its chromicyanide, and (11) cobalticyanide; (12) thiocyanate, and (13) its chromithiocyanate; and (14) dichromate.

(iii) *Hexacarbamides*, or *hexaurea salts*, $[Cr(NH_2.CO.NH_2)_6]X_3$. W. J. Sell, M. Kilpatrick, P. Pfeiffer, A. Werner and D. Kalkmann, G. A. Barbieri, and J. Meyer and L. Speich, E. Wilke-Dörfurt and co-workers studied these salts, and reported: (1) the chloride, and its complex (2) with mercuric chloride, and (3) with platinic chloride; (4) bromide; (5) perbromide; (6) iodide; (7) periodide; (8) chlorate; (9) perchlorate; (10) hexasulphide; (11) sulphate; (12) hydrosulphate; (13) chlorosulphate; (14) bromosulphate; (15) perbromosulphate; (16) iodosulphate; (17) periodosulphate; (18) chloratosulphate; (19) perchlorate; (20) perchloratosulphate; (21) persulphate; (22) fluosulphonate; (23) sulphatofluosulphonate; (24) thiosulphate; (25) selenate; (26) periodocarbonate; (27) nitrite; (28) sulphatonitrite; (29) cobaltinitrite; (30) diamminotetranitritocobaltiate; (31) chlorodiamminotetranitritocobaltiate; (32) nitrate; (33) sulphatonitrate; (34) cyanide; (35) thiocyanate; (36) ferrocyanide; (37) ferricyanide; (38) nitroprusside; (39) manganicyanide; (40) cobalticyanide; (41) chloronickelocyanide; (42) chloroplatinocyanide; (43) hexathiocyanatochromiate; (44) hexacyanochromiate; (45) fluosilicate; (46) fluoborate; (47) fluoboratosulphate; (48) chromate; (49) chlorochromate; (50) dichromate; (51) chlorodichromate; (52) bromodichromate; (53) perchloratodichromate; (54) disulphatodichromate; (55) nitratodichromate; (56) tetrafluoboratodichromate; (57) permanganate; (58) sulphatopermanganate; (59) dichromatopermanganate; (60) oxalate; (61) picrate; (62) naphthalene-2-sulphonate; (63) toluenesulphonate; (64) *o*-dichlorobenzenesulphonate; (65) sulphatobenzenesulphonate; and (66) diflavianate-flavianate. E. Wilke-Dörfurt and R. Pfau studied the isomorphism of the permanganate, perchlorate, fluoborate, fluosulphonate, and iodide.

(iv) *Bisethylenediaminopropylenediamines*, $[Cr\ en_2pn]X_3$. These salts were studied by P. Pfeiffer, P. Pfeiffer and H. Pietsch, and P. Pfeiffer, T. Gassmann. They include: (1) bromide; (2) iodide; (3) oxalate and (4) its chromioxalate, and (5) cobaltioxalate; (6) cyanide, and its (7) chromicyanide, and (8) cobalticyanide; and (9) thiocyanate.

(v) *Trispropylenediamines*, $[Cr\ pn_3]X_3$. These salts were studied by P. Pfeiffer and M. Haimann, and P. Pfeiffer and T. Gassmann. They include: (1) iodide; (2) cobaltioxalate; (3) chromicyanide; (4) cobalticyanide; (5) thiocyanate; and (6) chromithiocyanate.

(vi) *Aquopentammines*, $[Cr(NH_3)_5(H_2O)]X_3$. These salts are the so-called

*chromium roseo-salts*, studied by S. M. Jörgensen, F. Ephraim and W. Ritter, A. Benrath, O. Hassel and G. B. Næss, A. Hiendlmayr, and O. T. Christensen. They include: (1) hydroxide; (2) fluoride—*vide supra*, (3) chloride, and (4) its mercurichloride; (5) bromide, and (6) its bromoplatinate; (7) iodide; (8) perchlorate; (9) sulphate, and (10) its chloroplatinate; (11) nitrate, and (12) hydronitrate; (13) cyanide, and (14) its chromicyanide, (15) its ferricyanide, and (16) its cobalticyanide. H. J. S. King showed that these salts may be hydroxypentammines.

(vii) *Diaquotetrammines*, $[Cr(NH_3)_4(H_2O)_2]X_3$. These salts were investigated by P. Pfeiffer. They include: (1) hydronitrate; (2) chloride; and (3) bromide.

(viii) *Diaquobisethylenediamines*, $[Cr\ en_2(H_2O)_2]X_3$. These salts were studied by P. Pfeiffer. These are the isomeric forms:

(*a*) *Cis-salts*, including (1) chloride; (2) bromide; (3) chromioxalate; and (4) chromithiocyanate.

(*b*) *Trans-salts*, including (1) chloride; and (2) bromide.

(ix) *Triaquotriammines*, $[Cr(NH_3)_3(H_2O)_3]X_3$. These salts were studied by A. Werner, S. Guralsky, and E. H. Riesenfeld and F. Seemann and they include: (1) the chloride; (2) the perchlorate; (3) the bromide; (4) hydroxyiodide; and (5) chloronitrate.

(x) *Tetraquodiammines*, $[Cr(NH_3)_2(H_2O)_4]X_3$. These salts were studied by A. Werner and J. Klein. They include: (1) chloride; (2) bromide; (3) sulphate.

(xi) *Tetraquodipyridines*, $[Crpy_2(H_2O)_4]X_3$. These salts were studied by P. Pfeiffer, P. Pfeiffer and W. Osann, and P. Pfeiffer and M. Tapuach. They include: (1) chloride; (2) bromide; (3) sulphate, and (4) hydrosulphate; (5) nitrate; and (6) chromicyanide.

(xii) *Diaquotetramido-salts*, $[Cr(H_2O)_2(C_2H_5O_2N)_4]$, studied by G. Florence and E. Couture.

(xiii) *Hexaquo-salts*, $[Cr(H_2O)_6]X_3$. These salts were studied by A. Werner and A. Gubser, A. Gubser, A. Werner and R. Huber, P. Pfeiffer, R. F. Weinland and R. Krebs, R. F. Weinland and T. Schumann, and L. A. Welo. They correspond with the hexahydrated chlorides, sulphates, and chlorosulphates. J. Meyer and L. Speich prepared the selenate.

(xiv) *Hexa-antipyrino-salts*, $[Cr(COC_{10}H_{12}N_2)_6]X_3$, were prepared by E. Wilke-Dörfurt and H. G. Mureck. For example, (1) the fluoborate, $[Cr(COC_{10}H_{12}N_2)_6](BF_4)_3$; (2) the permanganate; (3) the fluosulphonate; (4) the thiocyanate; (5) the dichromate; (6) the chlorate; (7) the thiosulphate; (8) the ferrocyanide; (9) the ferricyanide; and (10) the picrate.

(xv) *Trioxalato-salts*, $R_3'[Cr(C_2O_4)_3]$, studied by A. G. Berghman.

II.—**The pentammine family,** or compounds of the bivalent, basic group: $[CrA_5X]''$. P. Larisch made some comparative observations on the solubilities of these salts.

(i) *Hydroxypentammines*, $[Cr(NH_3)_5(OH)]X_2$. S. M. Jörgensen, P. Pfeiffer, A. Werner, A. Benrath, L. A. Welo, J. V. Dubsky, and H. J. S. King reported (1) chloride; (2) bromide; (3) iodide; (4) sulphate; (5) dithionate; (6) nitrate; (7) chromate; (8) oxalate; (9) picramate; (10) picrate; (11) dipicrylamide; and (12) 2 : 4-dinitro-$\alpha$-naphthoxide-$\gamma$-sulphonate. The (13) hydroxide was obtained by the action of silver oxide on the chloride.

(ii) *Hydroxyaquopentammines*, $[Cr(NH_3)_5(H_2O)(HO)]X_2$. These salts were studied by P. Pfeiffer. They include: (1) bromide; and (2) dithionate.

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(iii) *Hydroxyaquobisethylenediamines*, $[Cr\ en_2(H_2O)(HO)]X_2$. These salts were studied by P. Pfeiffer, P. Pfeiffer and R. Stern, P. Pfeiffer and R. Prade, P. Pfeiffer and T. G. Lando. There are isomeric forms:

(*a*) *Cis-salts*, including (1) chloride; (2) bromide; (3) iodide; and (4) dithionate.

(*b*) *Trans-salts*, including (1) bromide; (2) iodide and (3) dithionate.

(iv) *Hydroxydiaquotriammines*, $[Cr(NH_3)_3(H_2O)_2(HO)]X_2$ The iodide was studied by A. Werner.

(v) *Hydroxytriaquodiammines*, $[Cr(NH_3)_2(H_2O)_3(OH)]X_2$. The sulphate was studied by A. Werner and J. Klein, and A. Werner and V. Dubsky.

(vi) *Hydroxytriaquodipyridines*, $[Crpy_2(H_2O)_3(OH)]X_2$. These salts were studied by P. Pfeiffer, P. Pfeiffer and M. Tapuach, and P. Pfeiffer and W. Osann. They include: (1) chloride; (2) sulphate; and (3) thiocyanate.

(vii) *Nitritopentammines*, $[Cr(NH_3)_5(NO_2)]X_2$. They are the so-called *chromium xantho-salts*. These salts were studied by O. T. Christensen, J. N. Brönsted and A. Petersen, and A. Werner and A. Miolati. They include: (1) chloride, and (2) its mercurichloride, and (3) its chloroplatinate; (4) bromide; (5) iodide; (6) sulphate; (7) dithionate; (8) nitrate; (9) carbonate; (10) chromate; and (11) dichromate.

(viii) *Nitratopentammines*, $[Cr(NH_3)_5(NO_3)]X_2$. These salts were studied by A. Werner and J. von Halban. They include: (1) iodide and (2) nitrate.

(ix) *Nitratodiaquotriammines*, $[Cr(NH_3)_3(H_2O)_2(NO_3)]X_2$. The nitrate was studied by E. H. Riesenfeld and F. Seemann.

(x) *Fluopentammines*, $[Cr(NH_3)_5F]X_2$. These salts were prepared by A. Hiendlmayr. They include: (1) fluoride; (2) chloride; (3) nitrate; (4) chromate; and (5) ferricyanide.

(xi) *Chloropentammines*, $[Cr(NH_3)_5Cl]X_2$. These are the so-called *chromium purpureo-salts*. They were studied by O. T. Christensen, A. Werner and A. Miolati, O. Hassel and G. B. Næss, F. Ephraim and W. Ritter, J. Meyer and L. Speich, J. N. Brönsted and A. Petersen, H. J. S. King, L. A. Welo, and S. M. Jörgensen. They include: (1) chloride; (2) its mercurichloride, and (3) its chloroplatinate; (4) bromide, and (5) its mercuribromide; (6) iodide, and (7) its mercuriiodide; (8) chlorate; (9) perchlorate; (10) pentasulphide; (11) sulphate, and (12*a*) its hydrosulphate; (12*b*) selenate; (13) dithionate; (14) fluosilicate; (15) oxalate; (16) ferrocyanide; (17) chromate; (18) picrate; (19) 2 : 4-dinitro-$\alpha$-naphthoxide; (20) 2 : 4-dinitro-$\alpha$-naphthoxide-$\gamma$-sulphonate; and (21) 2 : 3 : 6-trinitrophenoxide.

(xii) *Chloroaquotetrammines*, $[Cr(NH_3)_4(H_2O)Cl]X_2$. These are the so-called *chromium roseo-salts*. They were studied by E. Frémy, P. T. Cleve, A. Werner and A. Miolati, S. M. Jörgensen, J. Petersen, P. Pfeiffer and S. Basci, P. Pfeiffer. They include: (1) chloride, and its (2) mercurichloride, and (3) its chloroplatinate; (4) bromide; (5) iodide; (6) sulphate; (7) nitrate; (8) fluosilicate; (9) oxalate; and (10) chromate.

(xiii) *Chlorodiaquotriammines*, $[Cr(NH_3)_3(H_2O)_2Cl]X_2$. These salts were studied by E. H. Riesenfeld and F. Seemann. They include: (1) chloride; and (2) sulphate.

(xiv) *Bromodiaquotriammines*, $[Cr(NH_3)_3(H_2O)_2Br]X_2$. These salts, prepared by S. Guralsky, include: (1) chloride; (2) bromide; and (3) sulphate.

(xv) *Chloropentaquo-salts*, $[Cr(H_2O)_5Cl]X_2$. These salts have been discussed in connection with the hydrates of chromic chlorides. They were discussed by N. Bjerrum, A. Recoura, R. F. Weinland and R. Krebs, and R. F. Weinland and T. Schumann. The series is represented by (1) chloride; (2) sulphate; and (3) chlorosulphate. J. Meyer and L. Speich made (4) the selenate.

(xvi) *Bromopentammines*, $[Cr(NH_3)_5Br]X_2$. These salts were studied by S. M. Jörgensen, and A. Werner and A. Miolati. They are represented by (1) chloride; (2) bromide, and (3) its bromoplatinate; (4) nitrate; and (5) chromate.

(xvii) *Bromoaquotetrammines*, $[Cr(NH_3)_4(H_2O)Br]X_2$. The salts were studied by P. T. Cleve, and P. Pfeiffer and S. Basci. They include: (1) chloride; (2) bromide; and (3) sulphate.

(xviii) *Bromoaquobisethylenediamines*, $[Cr\ en_2(H_2O)Br]X_2$. The salts were studied by P. Pfeiffer, P. Pfeiffer and R. Stern, and P. Pfeiffer and T. G. Lando. They include: (1) bromide; and (2) chromithiocyanate.

(xix) *Bromodiaquotriammines*, $[Cr(NH_3)_3(H_2O)_2Br]X_2$. A. Werner prepared (1) the chloride; (2) the bromide; and (3) the sulphate.

(xx) *Iodopentammines*, $[Cr(NH_3)_5I]X_2$. These salts were studied by A. Werner and A. Miolati, and S. M. Jörgensen. The salts include: (1) chloride, and (2) its chloroplatinate; (3) iodide; and (4) nitrate.

(xxi) *Iodoaquotetrammines*, $[Cr(NH_3)_4(H_2O)I]X_2$. P. T. Cleve prepared the iodide.

(xxii) *Thiocyanatopentammines*, $[Cr(NH_3)_5(SCy)]X_2$. The salts were studied by A. Werner and J. von Halban. The salts include: (1) chloride; (2) bromide; (3) nitrate; (4) thiocyanate; and (5) dichromate.

(xxiii) *Sulphatopentaquo-salts*, $[Cr(H_2O)_5(SO_4)]X_2$. The chloride was prepared by R. F. Weinland and T. Schumann.

III.—**The tetrammine family,** or compounds of the univalent basic group: $[CrA_4X'X']$. P. Larisch made some comparative observations on the solubilities of these salts.

(i) *Dihydroxydiaquodiammines*, $[Cr(NH_3)_2(H_2O)_2(OH)_2]X$. These salts were prepared by A. Werner and J. V. Dubsky, and A. Werner and J. L. Klein. The salts include: (1) chloride; (2) bromide; (3) iodide; (4) dithionate; and (5) thiocyanate.

(ii) *Dihydroxydiaquodipyridines*, $[Crpy_2(H_2O)_2(HO)_2]X$. These salts were prepared by P. Pfeiffer, P. Pfeiffer and W. Osann, and P. Pfeiffer and M. Tapuach. The salts include: (1) chloride; (2) bromide; (3) iodide; (4) sulphate; (5) nitrate; and (6) thiocyanate.

(iii) *Dichlorotetraquo-salts*, $[Cr(H_2O)_4Cl_2]X$, represented by J. Meyer and L. Speich's $[Cr(H_2O)_4Cl_2](SeO_4)_2[Cr(H_2O)_6]$. The salts are represented by the (1) chloride and its complexes with (2) antimonic chloride, and (3) cæsium chloride; as well as by the (4) sulphate. They were studied by A. Werner and A. Gubser, N. Bjerrum, R. F. Weinland and K. Feige, O. Stelling, and P. Pfeiffer.

(iv) *Dihydroxydiaquoethylenediamines*, $[Cr(H_2O)_2\ en(OH)_2]X$. These salts, prepared by E. Weinmann, include: (1) chloride; (2) perchlorate; (3) bromide; (4) iodide; (5) dithionate; and (6) thiocyanate.

(v) *Dichlorobisethylenediamines*, $[Cr\ en_2Cl_2]X$. These salts were studied by A. Werner, P. Pfeiffer, P. Pfeiffer and P. Koch, P. Pfeiffer and T. G. Lando, P. Pfeiffer and R. Stern, and P. Pfeiffer and A. Trieschmann. There are the isomeric forms:

(*a*) *Inactive salts*, including (1) chloride and (2) its antimonichloride, and (3) chloroplatinate; (4) bromide; (5) iodide; (6) sulphate; (7) dithionate; (8) nitrate; and (9) thiocyanate.

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(*b*) *Dextro-cis salts*, including (1) chloride; (2) bromide, and (3) its bromocamphorsulphonate; and (4) nitrate.

(*c*) *Lævo-cis-salts*, including (1) chloride; (2) bromide, and (3) its bromocamphorsulphonate; and (4) nitrate.

(*d*) *Trans-salts*, including (1) chloride, and (2) its hydrochloride, and (3) chloroplatinate; (4) bromide; (5) iodide; (6) dithionate; (7) nitrate; (8) chromidioxalatoethylenediamine; and (9) thiocyanate.

(vi) *Dichloroaquotriammines*, $[Cr(NH_3)_3(H_2O)Cl_2]X$. These salts were prepared by A. Werner, F. Frowein, E. H. Riesenfeld and F. Seemann, and S. Guralsky, and include: (1) chloride; (2) iodide; (3) sulphate: (4) hydrosulphate; and (5) nitrate.

(vii) *Dibromoaquotriammines*, $[Cr(NH_3)_3(H_2O)Br_2]X$. These salts, prepared by S. Guralsky, include: (1) bromide; (2) iodide; (3) sulphate; (4) nitrate; and (5) thiocyanate.

(viii) *Dichlorodiaquodiammines*, $[Cr(NH_3)_2(H_2O)_2Cl_2]X$. A. Werner and J. L. Klein prepared the chloride.

(ix) *Dichlorodiaquodipyridines*, $[Crpy_2(H_2O)_2Cl_2]X$. These salts were prepared by P. Pfeiffer and M. Tapuach, and include: (1) chloride, and (2) its complex with pyridinium chloride; (3) bromide; and (4) nitrate.

(x) *Dibromotetraquo-salts*, $[Cr(H_2O)_4Br_2]X$. These salts are represented by the chloride prepared by N. Bjerrum.

(xi) *Dibromobisethylenediamines*, $[Cr\,en_2Br_2)X$. They were studied by P. Pfeiffer, and P. Pfeiffer and A. Trieschmann. There are isomeric forms:

(*a*) *Cis-salts*, including (1) bromide; (2) iodide; and (3) dithionate.

(*b*) *Trans-salts*, including (1) bromide and (2) its hydrobromide, and (3) its mercuribromide; (4) iodide; (5) dithionate; (6) nitrate; and (7) thiocyanate.

(xii) *Dichloroaquotriammines*, $[Cr(NH_3)_3(H_2O)Cl_2]X$. The chloride was studied by E. H. Riesenfeld and F. Seemann.

(xiii) *Dibromodiaquodiammines*, $[Cr(NH_3)_2(H_2O)_2Br_2]X$. A. Werner and J. L. Klein, and A. Werner and J. V. Dubsky studied the bromide.

(xiv) *Dibromodiaquopyridines*, $[Cr(NH_3)_2(H_2O)_2Br_2]X$. These salts were studied by A. Werner and A. Gubser, and P. Pfeiffer and M. Tapuach. The salts include: (1) bromide; (2) iodide; and (3) nitrate.

(xv) *Dibromotetraquo-salts*, $[Cr(H_2O)_4Br_2]X$. These salts were studied by A. Recoura, A. Werner and A. Gubser, A. Werner and R. Huber, P. Pfeiffer and M. Tapuach, and N. Bjerrum. The salts include: (1) chloride; (2) bromide; (3) sulphate; and (4) the cobaltic tetranitritodiammine.

(xvi) *Diiodobisethylenediamines*, $[Cr\,en_2I_2]X$. The double salt with mercuric iodide was studied by P. Pfeiffer and T. G. Lando.

(xvii) *Dithiocyanatotetrammines*, $[Cr(NH_3)_4(SCy)_2]X$. These salts were studied by P. Pfeiffer and M. Tilgner, and A. Werner and J. von Halban. The salts include: (1) chloride; (2) bromide; (3) sulphate; (4) nitrate; and (5) thiocyanate.

(xviii) *Dithiocyanatobisethylenediamines*, $[Cr\,en_2(SCy)_2]X$. These salts were studied by P. Pfeiffer and M. Haimann, P. Pfeiffer and P. Koch, P. Pfeiffer and R. Stern, and P. Pfeiffer. There are isomeric forms:

(*a*) *Cis-salts*, including (1) chloride; (2) bromide; (3) iodide and its complex with mercuric iodide; (4) sulphate; (5) nitrate; (6) thiocyanate; and (7) chromithiocyanate.

(*b*) *Trans-salts*, including (1) chloride; (2) bromide, (3) sulphate; (4) nitrate; (5) thiocyanate; and (6) chromithiocyanate.

(xix) *Oxalatotetrammines*, $[Cr(NH_3)_4(C_2O_4)]X$. These salts were studied by P. Pfeiffer and S. Basci. The salts include : (1) chloride ; (2) bromide ; (3) iodide ; (4) nitrate ; and (5) chromidioxalatodiammine.

(xx) *Oxalatobisethylenediamines*, $[Cr\ en_2(C_2O_4)]X$. These salts were studied by P. Pfeiffer, P. Pfeiffer and R. Stern, and P. Pfeiffer and A. Trieschmann, and H. Schwarz. The salts include : (1) bromide ; (2) iodide ; (3) chromidioxalatoethylenediamine ; and (4) the chromidioxalatodiaquo-salt. Some other oxalato-salts were studied by R. Weinland and W. Hübner, and F. Hans.

IV.—**The triammine family,** or compounds of the null-valent group : $[CrA_3X_3']$.

(i) *Trichlorotriammine*, $[Cr(NH_3)_3Cl_3]$, was prepared by A. Werner, E. H. Riesenfeld and F. Seemann, F. Frowein, O. Stelling, S. Guralsky, and H. I. Schlesinger and co-workers. There are also the tribromide and the mixed chlorobromides.

(ii) *Trihydroxyaquodiammines*, $[Cr(NH_3)_2(H_2O)(OH)_3]$. The *tetrahydrate* was studied by A. Werner and J. L. Klein.

(iii) *Trihydroxyaquodipyridines*, $[Crpy_2(H_2O)(OH)_3]$. The *hexahydrate* was studied by P. Pfeiffer and M. Tapuach.

(iv) *Dichlorohydroxyaquodipyridine*, $[Crpy_2(H_2O)Cl_2]$. This salt was prepared by P. Pfeiffer and M. Tapuach.

(v) *Trichlorotripyridine*, $[Crpy_3Cl_3]$. This salt was examined by P. Pfeiffer. The addition products with (1) $2CH_3Cy$, and (2) $C_2H_5Cy$ were examined by P. Pfeiffer.

(vi) *Trichloroaquodipyridine*, $[Crpy_2(H_2O)Cl_3]$. This salt was studied by P. Pfeiffer and M. Tapuach.

(vii) *Triaquotrichlorides*, $[Cr(H_2O)_3Cl_3]$. The addition product with 2Py.HCl was studied by P. Pfeiffer.

(viii) *Trisethylalcoholotrichloride*, $[Cr(C_2H_5.OH)_3Cl_3]$. This compound was examined by I. Koppel.

(ix) *Trichlorotrithiourea*, $[Cr(CSN_2H_4)_3Cl_3]$. *The hemihydrate* was examined by P. Pfeiffer.

(x) *Triaquotribromides*, $[Cr(H_2O)_3Br_3]$. The addition product with 2PyHBr was studied by P. Pfeiffer.

(xi) *Trithiocyanatotriammine*, $[Cr(NH_3)_3(SCy)_3]$. This compound was studied by A. Werner and J. von Halban.

(xii) *Trithiocyanatoaquodiammines*, $[Cr(NH_3)_2(H_2O)(SCy)_3]$. The monohydrate was studied by O. Nordenskjöld, J. A. Siemssen, and A. Werner and G. Richter ; (1) the addition product with (2) ethylenediammine, (3) piperidine ; (4) aniline, (5) brucine ; and (6) pyridine were studied by O. Nordenskjöld, and J. A. Siemssen.

(xiii) *Dichlorothiocyanatotriammine*, $[Cr(NH_3)_3(SCy)Cl_2]$. This salt was prepared by S. Guralsky.

V.—**The diammine family,** or compounds of the univalent, acidic group : $[CrA_2X_4]$.

(i) *Tetrathiocyanatodiammines*, $[Cr(NH_3)_2(SCy)_4]M$. These compounds were studied by J. Morland, A. Reinecke, P. T. Cleve, O. Nordenskjöld, R. Escales and H. Ehrensperger, J. A. Siemssen, E. Orloff, O. T. Christensen, A. Werner and G. Richter, A. Werner and J. L. Klein, and P. Pfeiffer and M. Tilgner. The compounds include : (1) the acid and its monohydrate or dihyrate ; (2) sodium ; (3) potassium—*Reinecke's salt*—and (4) its complex with potassium iodide ; (5) rubidium, and (6) a complex with pyridine ; (7) cæsium, and (8) a complex with pyridine ; (9) copper ; (10) barium ; (11) zinc, (12) a complex with pyridine ; and (13) one with ammonia ; (14) cadmium ; (15) mercury ; (16) iron ; (17) cobalt ; (18) ammonium and (19) its hydrate, and (20) iodide ; (21) nitrosyl ; (22) guanidine ; (23) methylamine : (24) dimethylamine ; (25) trimethylamine ;

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(26) ethylamine; (27) amylamine; (28) tetramethylammonium; (29) methylpyridinium; (30) methylquinolinium; (31) *m*-xylidinium; (32) ethylenediamine; (33) pentamethylenediamine; (34) aniline; (35) ammonium aniline; (36) *o*-toluidine; (37) *p*-toluidine; (38) phenylhydrazine; (39) piperidine; (40) pyridine; (41) picoline; (42) quinoline; (43) morphine; (44) quinine; (45) strychnine; (46) pilocarpine; and (47) cocaine.

(ii) *Tetrathiocyanatodipyridines*, $[CrPy_2(SCy)_4]M$. These compounds were studied by J. Sand and O. K. H. Burger, and P. Pfeiffer and W. Osann. The salts include: (1) potassium—the dihydrate, and tetrapyridine; (2) sodium—the trihydrate, and tetrapyridine; and (3) the mono- and di-pyridines.

(iii) *Tetrathiocyanatoethylenediamine*, $[Cr\ en(SCy)_4]M$. These compounds, prepared by E. Weinmann, include: (1) sodium; (2) potassium; (3) cæsium; (4) ammonium; (5) caffeine; (6) coniine; (7) nicotine; (8) narcotine; (9) codeïne; (10) strychnine; and (11) brucine.

(iv) *Dioxalatodiammines*, $[Cr(NH_3)_2(C_2O_4)_2]M$. P. T. Cleve, and P. Pfeiffer and S. Basci studied the complex which the group forms with chromic oxalatotetrammine.

(v) *Dioxalatoethylenediamines*, $[Cr\ en(C_2O_4)_2]M$. These salts were studied by H. Schwarz, P. Pfeiffer, P. Pfeiffer and A. Trieschmann, P. Pfeiffer and R. Stern, and P. Pfeiffer and R. Prade. The salts include: (1) potassium and its complex with potassium iodide; (2) the addition product with chromic *trans*-dichlorobisethylenediamine; (3) the addition product with chromic oxalatobisethylenediamine; (4) the addition product with cobaltic dichlorobisethylenediamine, and its dihydrate.

(vi) *Dioxalatodiaquo-salts*, $[Cr(H_2O)_2(C_2O_4)_2]M$. The (1) ammonium; (2) sodium; and (3) potassium salts were studied by A. Rosenheim and L. Cohn, and P. Pfeiffer and R. Stern.

VI.—**The monammine family,** or compounds of the bivalent, acidic group: $[CrAX_5]$. These compounds are represented by the pentahalides—*vide supra*—studied by A. Werner, and A. Werner and A. Gubser—*e.g.*, (1) $M_2[Cr(H_2O)F_5]$; (2) $M_2[Cr(H_2O)Cl_5]$; and (3) $M_2[Cr(H_2O)Br_5]$.

VII.—**The hexa-acid family** or compounds of the tervalent, acidic group: $[CrX_6]$. These compounds are represented by (1) $M_3[CrF_6]$; (2) $M_3[CrCy_6]$; (3) $M_3[Cr(SCy)_6]$; and (4) $M_3[Cr(C_2O_4)_3]$, studied by H. Schwarz, L. A. Welo, P. Pfeiffer, and J. A. Siemssen.

*B.—Polychromic compounds, that is, compounds with more than one chromium atom in the nucleus.*

I.—**Dichromic salts**—with two chromium atoms in the nucleus. Some salts prepared by P. Schützenberger in 1868—*viz.* $[Cr_2O(CH_3COO)_3(NO_3)]$; $[Cr_2(CH_3COO)_4(NO_3)(OH)]$; and $[Cr_2(CH_3COO)_5.NO_3]$ may belong to this group. There are also salts of the type $[Cr_2(OH)(OOC.CH_2SCy)_4]X$, described by R. G. Krasnowskaja including the hydroxide, chloride, bromide, iodide, sulphate, and dithionate; and D. R. Camhi's $[Cr_2(OOC.CH_2Cy)_6OH]X$.

(i) *Hydroxydecammines*, $[Cr_2(OH)(NH_3)_{10}]X_5$. These salts were studied by S. M. Jörgensen, A. Werner, J. Petersen, and P. Pfeiffer. S. M. Jörgensen called them the *chromium rhodo-salts*; and A. Werner, *decammine-ol-dichromic salts*. The rhodo-salts include: (1) chloride, (2) its chloraurate, and (3) its chloroplatinate; (4) bromide, and (5) its bromoplatinate; (6) iodide; (7) sulphate; (8) dithionate; and (9) nitrate. These salts have a neutral reaction; and A. Werner represented them by the following formula in order to show their

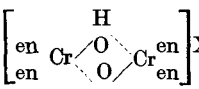
relationship with the isomeric erythro-salts—*vide infra*—which have an acidic reaction :

Rhodo-salts. Erythro-salts.

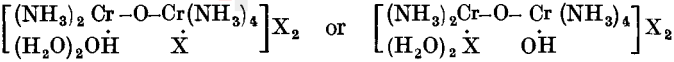
There are the so-called *basic rhodo-salts*, $[Cr_2(OH)(NH_3)_{10}]X_4(OH)$, studied by S. M. Jörgensen, and A. Werner. They are represented by (1) chloroiodide ; (2) bromide ; and (3) dithionate. The rhodo-salts are isomeric with the *erythro-salts* studied by S. M. Jörgensen, and represented by (1) chloroiodide ; (2) chloroplatinate ; (3) bromide ; (4) sulphate ; and (5) nitrate.

(ii) *Oxydecammines*, $[Cr_2O(NH_3)_{10}]X_4$, or $[(NH_3)_3Cr{-}O{-}Cr(NH_3)_5]X_4$. They were studied by S. M. Jörgensen, and A. Werner. The former called them *basic chromium erythro-salts*. They include : (1) bromide ; (2) dithionate ; and (3) nitrate.

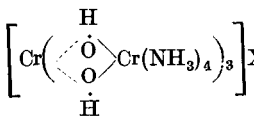
(iii) *Dihydroxyaquatorethylenediamines*, $[Cr_2(OH)_2\,en_4]X_4$. They were studied by P. Pfeiffer and R. Stern. The salts include : (1) bromide ; and (2) iodide. P. Pfeiffer represented them by the formula :



(iv) *Trihydroxyaquohexammines*, $[Cr_2(OH)_3(H_2O)(NH_3)_6]X_3$, or possibly $[Cr_4(OH)_6(NH_3)_{12}]X_6$. S. M. Jörgensen studied these salts and called them *chromium rhodoso-salts*. They were also studied by P. Pfeiffer, and J. Petersen. The salts include : (1) chloride, (2) its chloraurate, and (3) its chloroplatinate ; (4) bromide ; (5) iodide ; (6) polysulphide ; (7) sulphate ; (8) hydrosulphate ; (9) hydroxalate ; and (10) chromate. S. M. Jörgensen gave for the formula :



and P. Pfeiffer :



II.—**Trichromic salts** having three chromium atoms in the nucleus. Series of complex acetates, cyanoacetates, bromo-acetates, etc., were described by D. R. Camhi, J. A. Jwanowits, R. F. Weinland, G. Aschkinasy, and R. G. Krasnowskaja. In illustration, there are :

(i) *Hexacetatodihydroxytriammines*, $[Cr_3(CH_3COO)_6(OH)_2(NH_3)_3]X$, represented by the iodide prepared by R. F. Weinland and E. Büttner, and L. A. Welo.

(ii) *Hexacetatodihydroxytripyridines*, $[Cr_3Py_3(CH_3COO)_6(OH)_2]X$. These salts, prepared by R. F. Weinland and E. Gussmann, and L. A. Welo are represented by (1) hydroxystannichloride ; (2) chloroplatinate ; (3) iodide ; (4) nitrate ; (5) acetate ; (6) chloracetate ; (7) nitratacetate ; (8) ferricyanide ; (9) complex chromichromatodichromate ; and (10) permanganate.

(iii) *Chromic pentahydroxyaquodecammino-salts*, $[Cr_3(OH)_5(NH_3)_{10}(H_2O)](S_2O_3)_2.nH_2O$, and *chromic pentahydroxydiaquo-enneammino-salts*, *e.g.* $[Cr(OH)_5(NH_3)_9(H_2O)_2](S_2O_3)_2.3H_2O$ of P. Ray and P. B. Sarkar.

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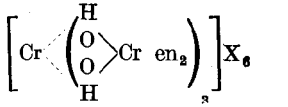
(iv) *Hexaformatodihydroxy-salts*, studied by L. A. Welo, R. Weinland and J. Lindner, etc.

(v) *Hexapropionatohydroxyfluoro-salts*, investigated by R. Weinland and J. Lindner.

III.—**Tetrachromic salts** having four chromium atoms in the nucleus.

(i) *Hexahydroxydodecammines—vide supra, trihydroxyaquohexammines.*

(ii) *Hexahydroxysexiesethylenediamines*, $[Cr_4(OH)_6\,en_6]X_6$. They were studied by P. Pfeiffer, and P. Pfeiffer and W. Vorster. The salts include: (1) chloride; (2) bromide; (3) iodide, and (4) its mercuri-iodide; (5) sulphate; (6) dithionate; (7) nitrate; (8) thiocyanate; and (9) chromate. P. Pfeiffer represented the constitution by the formula:



About a dozen and a half salts, which have been reported, have not been fitted into A. Werner's system. When the salts are investigated more closely it may be possible to do something more with them. P. T. Cleve reported a *chromic tetramminosulphate*, $2Cr_2O_3.SO_3.4NH_3.24H_2O$; *chromic tetramminodinitrate*, $Cr_2O_3.N_2O_5.4NH_3.3H_2O$, *chromic diamminonitrate*, $2Cr_2O_3.N_2O_5.4NH_3.nH_2O$; and *ammonium chromic heptamminoctonitrate*, $2Cr(NO_3)_3.7NH_3.2NH_4NO_3.4\frac{1}{2}H_2O$; the *chromic diamminoxalate*, $Cr_2O_3.C_2O_3.2NH_3.8H_2O$, and *ammonium chromic hexamminotrioxalate*, $Cr_2(C_2O_4)_3.6NH_3.(NH_4)HCr_2O_4.1\frac{1}{2}H_2O$; and the *chromic heptamminonitratooxalate*, $2Cr(NO_3)(C_2O_4).7NH_3.3H_2O$; W. R. Lang and E. H. Jolliffe, *chromic quinquiesmethylaminotrichloride*, $CrCl_3.5CH_3NH_2$; W. R. Lang and C. M. Carson, *chromic quinquiesethylaminotrichloride*, $CrCl_3.5C_2H_5NH_2.H_2O$, and *chromic quaterethylamine*, $CrCl_3.4C_2H_5NH_2.H_2O$; and *chromic quaterethylenediaminotrichloride*, $CrCl_3.4C_2H_4(NH_2)_2H_2O$; O. Nordensjöld, *mercuric chromic sulphotrithiocyanatodiammine*, $Cr(SCy)_3(NH_3)_2.6HgS$; J. Sand and O. K. H. Burger, *chromic oxytetrathiocyanatotetrammine*, $Cr_2O(SCy)_4(NH_3)_4$; and *chromic oxytetrathiocyanatotetrapyridine*, $Cr_2O(SCy)_4Py_4$; E. A. Werner, *oxalatotriamminochromic acid*, $HCr(C_2O_4)_2(NH_3)_3.3H_2O$; *potassium oxalatotriamminochromate*, $KCr(C_2O_4)_2(NH_3)_3.3H_2O$; and *ammonium oxalatotriamminochromate*, $(NH_4)_5Cr_4(C_2O_4)_5(NH_3)_3.14H_2O$.

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## § 25. The Complex Salts of Chromic Chloride

S. M. Jörgensen[1] treated mercuric chromic hexamminochloride—made by adding mercuric chloride to a hydrochloric acid soln. of chromic hexamminonitrate—with hydrogen sulphide, and obtained a liquid from which yellow crystals of **chromic hexamminotrichloride,** $[Cr(NH_3)_6]Cl_3.H_2O$, were obtained. The salt is freely soluble in water; and when treated with hydrochloric acid, it forms the chloropentamminodichloride, $[Cr(NH_3)_5Cl]Cl_2$. W. Biltz and E. Birk gave 1·585

for the sp. gr. of the hexammine at 25°/4° and 175·8 for the mol. vol. Y. Shibata measured the absorption spectrum. S. Aoyama and co-workers studied the X-ray absorption and constitution. A. Werner and A. Miolati found that a mol of the salt in $v$-litres of water at 25° had the mol. conductivity $\mu$ ;

| $v$ | 125 | 250 | 500 | 1000 | 2000 |
|---|---|---|---|---|---|
| $\mu$ | 353·5 | 388·6 | 418·8 | 441·7 | 463·6 mhos. |

E. Birk studied the mol. vol. of the ammonia in the ammines. H. J. S. King calculated 180·0 for the ionic mobility at 0° and 370·2 at 25°. F. Ephraim and P. Mosimann discussed the solubilities of the hexammines; O. Stelling, the X-ray spectrum; and H. Lessheim and co-workers, the electronic structure. A. Benrath found that in the presence of hydrochloric acid the stable phase is $[Cr(NH_3)_5Cl]Cl_2$. P. Pfeiffer also prepared *chromic trisethylenediaminotrichloride*, $[Cr\,en_3]Cl_3,3\frac{1}{2}H_2O$. O. T. Christensen obtained **chromic aquopentamminotrichloride,** $[Cr(H_2O)(NH_3)_5]Cl_3$, from a soln. of the base in hydrochloric acid. S. M. Jörgensen also prepared this salt. The orange-yellow crystals are freely soluble in water. The dil. aq. soln. is decomposed when boiled, but the acidified soln. is more stable. When boiled with hydrochloric acid, the chloropentamminochloride is formed. All three chlorine atoms are immediately precipitated by the addition of silver nitrate. F. Ephraim and W. Ritter obtained the salt by the action of an ammoniacal soln. of ammonium nitrate on potassium or ammonium chromic chloride. H. J. S. King also prepared this salt; and he gave for the conductivity, $\mu$ mhos, of a mol. of the salt in $v$ litres at 0° :

| $v$ | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|
| $\mu$ | 169·5 | 186·3 | 197·6 | 218·4 | 232·9 | 247·8 |

For the mol. conductivity, $\mu$, of soln. of a mol of the salt in $v$ litres of water at 25°, A. Werner and A. Miolati gave :

| $v$ | 125 | 250 | 500 | 1000 | 2000 |
|---|---|---|---|---|---|
| $\mu$ | 221·0 | 239·3 | 252·0 | 261·0 | 271·6 |

Values were also obtained by H. J. S. King who gave 174·3 for the ionic mobility at 0° of the $[Cr(NH_3)_5(H_2O)]^{\cdots}$-ion. F. Ephraim and W. Ritter found that the salt absorbs ammonia at a low temp., and the decomposition curve shows breaks corresponding with a tetrammine, and doubtful breaks for the hexammine and diammine. A. Benrath found that the stable phase in the presence of hydrochloric acid is $[Cr(NH_3)_5Cl]Cl_2$. P. Pfeiffer prepared **chromic diaquotetramminotrichloride,** $[Cr(H_2O)_2(NH_3)_4]Cl_3$, from a hydrochloric acid soln. of chromic hydroxyaquotetramminodithionate. The brick-red crystalline powder is soluble in water. The conc. aq. soln. gives an orange-red precipitate with potassium cobalticyanide and a brick-red precipitate with conc. hydrochloric or hydrobromic acid. Silver nitrate precipitates all three chlorine atoms. The salt gradually passed into the aquochlorotetramminodichloride. E. H. Riesenfeld and F. Seemann, and F. Frowein prepared **chromic triaquotriamminotrichloride,** $[Cr(NH_3)_3(H_2O)_3]Cl_3$, by dissolving chromic tetroxytriammine in dil. hydrochloric acid and passing hydrogen chloride into the resulting soln. After a time, bright red, needle-shaped crystals of the triaquotriamminotrichloride separate. If the hydrogen chloride is passed in for too long a time, the soln. becomes green in colour, and crystals of either the dichromic or the grey dichloroaquotriamminochloride, are obtained. A. Werner obtained the salt by dissolving chromium triamminotetroxide in hydrochloric acid (1 : 4) and saturating the cold soln. with hydrogen chloride; he also obtained it by covering a mixture of a gram of dichloroaquotriamminochloride and 8 c.c. of water with 5 c.c. of pyridine, and adding solid potassium iodide; the resulting chromium triamminotriaquohydroxyiodide is treated with conc. hydrochloric acid, and the resulting triamminotriaquotrichloride is purified by passing hydrogen chloride through the aq. soln. F. Frowein found that the dichloroaquo-

triamminochloride in aq. soln. gradually changes into the chlorodiaquotriamminodichloride ; and this, in turn, into the triaquotriamminotrichloride. The changes can be followed by the change of colour of the soln., that of the monoaquo-salt being blue, that of the diaquo-salt reddish-violet, and that of the triaquo-salt red. These changes are more rapid the more dil. the soln. The conductivity of the monoaquo-compound is lowest, that of the triaquo-compound highest, so that the change is accompanied by a gradual increase in conductivity of the soln. No direct transformation of the mono- into the tri-aquo-salt occurs, but the diaquo-salt is always the first hydration product of the monoaquo-compound. The measurements agree with the hypothesis that the compounds contain no water outside the inner sphere, that is, they are purely co-ordinated compounds. The soln. of the triaquo-compound undergoes slow decomposition, the conductivity curve first showing a maximum, followed by a minimum. Deposition of chromium hydroxide eventually takes place, but intermediate complex compounds are probably first formed. A. Werner also prepared **chromium triamminotriaquodichloronitrate,** $[Cr(H_2O)_3(NH_3)_3]Cl_2(NO_3)$, and also **chromium triamminotriaquotriperchlorate,** $[Cr(H_2O)_3(NH_3)_3](ClO_4)_3$.

P. Pfeiffer and R. Stern prepared **chromic cis-diaquobisethylenediaminotrichloride,** $[Cr\ en_2(H_2O)_2]Cl_3.2H_2O$, and P. Pfeiffer and R. Prade obtained the **trans-salt ;** A. Werner and J. L. Klein obtained **chromic tetraquodiamminotrichloride,** $[Cr(H_2O)_4(NH_3)_2]Cl_3$, from a hydrochloric acid soln. of the bromide. The pale red, monoclinic prisms are freely soluble in water, and insoluble in alcohol. P. Pfeiffer, and P. Pfeiffer and M. Tapuach prepared **chromic tetraquodipyridinotribromide,** $[CrPy_2(H_2O)_4]Br_3.2H_2O$. The preparation of **chromic hexaquotrichloride,** $[Cr(H_2O)_6]Cl_3$, by N. Bjerrum, A. Werner and A. Gubser, A. Werner and R. Huber, A. Weinland and R. Krebs, R. F. Weinland and T. Schumann, and P. Pfeiffer has been previously described.

H. J. S. King prepared rose-red needles of **chromic hydroxypentamminochloride,** $[Cr(NH_3)_5(OH)]Cl_2.H_2O$, by dissolving the aquopentamminochloride in conc. ammonia, and precipitating with alcohol. He gave for the conductivity, $\mu$ mho, of a mol of the salt in $v$ litres at 0° and 25° :

| $v$ | . | . | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|---|---|
| 0° | . | . | 108·8 | 119·0 | 127·5 | 134·9 | 138·8 | 147·2 |
| 25° | . | . | 206·2 | 225·7 | 239·0 | 253·0 | 261·9 | 274·6 |

He calculated 73·3 for the ionic mobility at 0° and 131·8 at 25°. P. Pfeiffer and R. Stern prepared **chromic cis-hydroxyaquobisethylenediaminodichloride,** $[Cr\ en_2(H_2O)(OH)]Cl_2.H_2O$ ; P. Pfeiffer, **chromic hydroxydiaquodipyridinodichloride,** $[CrPy_2(H_2O)_2(OH)]Cl_2$ ; and O. T. Christensen, **chromic nitritopentamminodichloride,** $[Cr(NH_3)_5(NO_2)]Cl_2$, by the action of dil. nitric acid on the chloride of the series. A. Werner and A. Miolati found the electrical conductivity of soln. with a mol of the salt in 125, 250, 500, 1000, and 2000 litres of water at 25° to be respectively $\mu$=221·0, 239·3, 252·0, 261·0, and 271·6.

S. M. Jörgensen prepared **chromic chloropentamminodichloride,** $[Cr(NH_3)_5Cl]Cl_2$, by reducing, say, 25 grms. of violet chromic chloride with hydrogen at a red-heat, and treating the product with a soln. of ammonium chloride in conc. aq. ammonia. Air is then passed through the blue liquid until oxidation is complete. Two litres of hydrochloric acid are added and the mixture is boiled for a few minutes when the salt separates as a carmine-red powder. This is washed with a mixture of hydrochloric acid (1 : 1), dissolved in dil. sulphuric acid, and filtered into a great excess of cold, conc. hydrochloric acid. The precipitate is boiled with hydrochloric acid, washed first with cold acid and water, then with alcohol, and finally dried in air at ordinary temp. F. Ephraim and W. Ritter obtained the salt by the action on potassium or ammonium chromic chloride of an ammoniacal soln. of ammonium nitrate. O. T. Christensen obtained it by reducing a soln. of potassium dichromate with alcohol and hydrochloric acid, and treated

the clear liquid in the absence of air with conc. hydrochloric acid and zinc. The blue liquid was then digested with ammonium chloride and conc. ammonia, and air passed through the liquor. The soln. was then boiled a short time with conc. hydrochloric acid. O. T. Christensen, and W. R. Lang and C. M. Carson also made the same salt by digesting violet chromic chloride with liquid ammonia. A. Werner and J. von Halban, S. M. Jörgensen, and O. T. Christensen also prepared this salt by the action of hydrochloric acid on some of the other chromic ammines. S. M. Jörgensen described the salt as a red crystalline powder consisting of octahedra of sp. gr. 1·687. R. Klement gave 1·696 for the sp. gr. and 143·7 for the mol. vol. Y. Shibata measured the absorption spectrum. A. Werner and A. Miolati found that a mol of the salt in $v$ litres of water at 25° has the mol. conductivity, $\mu$ :

| | | | | | |
|---|---|---|---|---|---|
| $v$ . . | 125 | 250 | 500 | 1000 | 2000 |
| $\mu$ . . | 221·7 | 239·0 | 250·5 | 260·2 | 269·9 |

H. J. S. King gave for the conductivity, $\mu$ mhos, of a mol of the salt in $v$ litres :

| | | | | | |
|---|---|---|---|---|---|
| $v$ . . | 64 | 128 | 256 | 512 | 1024 |
| $\mu$ 0° . . | 123·1 | 131·1 | 137·2 | 142·3 | 147·6 |
| $\mu$ 25° . . | 230·3 | 244·5 | 255·0 | 264·4 | 276·8 |

The ionic mobility at 0° is 75·2 and at 25°, 139·7. E. Rosenbohm found the magnetic susceptibility to be $25{\cdot}76\times10^{-6}$ mass units; and L. A. Welo gave $24{\cdot}80\times10^{-6}$. A. Benrath found that the salt is stable in the presence of hydrochloric acid. S. M. Jörgensen found that 100 grms. of water at 16° dissolve 0·65 grm. of the salt forming a violet-red soln. which, when exposed to light, deposits hydrated chromic oxide. When the soln. is kept in the dark, or boiled, it passes into the aquochlorotetramminodichloride. When the aq. soln. is boiled it forms the aquopentamminochloride; boiling soda-lye precipitates chromic hydroxide. The rate of hydrolysis of the salt was investigated by A. Werner and A. Miolati, A. B. Lamb and J. W. Marden, H. Freundlich and H. Pape, and H. Freundlich and R. Bartels. S. M. Jörgensen added that the aquochlorotetramminodichloride gives the following reactions: With sodium hypochlorite, nitrogen is evolved, and the chromium is oxidized to chromic acid. Its soln. gives a precipitate with conc. hydrochloric acid, owing to the insolubility of the chloride in acid. With hydrobromic acid, it gives a crystalline precipitate of the bromide, and with solid potassium iodide one of the iodide. When boiled with potassium cyanide, it turns yellow. Conc. nitric acid precipitates the chloro-nitrate. Hydrosilicofluoric acid throws down the red crystalline chlorofluosilicate. Platinic chloride precipitates, even from a very dil. soln., the chloropurpureochromium platinochloride. Sodium bromoplatinate gives an analogous precipitate. Mercuric chloride gives red needles of the double salt. Precipitates are also produced by potassium mercuric bromide and iodide, by sodium dithionate, potassium chromate, and dichromate, ammonium molybdate, and phosphomolybdate, and by picric and oxalic acids. In these respects this salt closely resembles the analogous cobalt salt. On treatment with silver nitrate only two atoms of chlorine are removed, and the chloro-nitrate is formed. By rubbing the solid chloride with silver oxide and water the aquochlorotetramminodichloride is formed. S. M. Jörgensen also prepared the sulphide, sulphate, hydrosulphate, dithionate, fluosilicate, nitrate, bromide, iodide, oxalate, ferrocyanide, and chromate, as well as complex mercury and platinic halides of the chromic chloropentammines. F. Ephraim and W. Ritter found that the chloropentamminodichloride does not absorb ammonia gas.

In 1858, E. Frémy obtained a salt which P. T. Cleve showed to be **chromic chloroaquotetramminodichloride,** $[Cr(NH_3)_4(H_2O)Cl]Cl_2$. It was prepared by allowing a sat. soln. of chromium chloride in aq. ammonia to stand in a closed

vessel until the liquid acquired a red colour ; it was then exposed to the air when it deposited a dark reddish-violet powder. The soln. of the salt in hydrochloric acid, when treated with an excess of conc. hydrochloric acid, furnished rose-red crystals of the aquochlorotetramminodichloride. S. M. Jörgensen obtained the salt by heating a conc. aq. soln. of 100 grms. of ammonium dichromate with 300 c.c. of hydrochloric acid of sp. gr. 1·17, 200 grms. of ammonium chloride, and 60–70 c.c. of alcohol, and evaporating to dryness. The product was digested for 24 hours with a litre of conc. ammonia ; the residue was dissolved in hydrochloric acid, and treated anew with ammonia. The ammoniacal soln. was mixed with 4 litres of conc. hydrochloric acid ; the precipitate was freed from ammonium chloride by hydrochloric acid (1 : 1). The mixture was dissolved in water and treated with a soln. of ammonium sulphate (1 : 5), and the precipitate washed with cold water ; and digested with hydrochloric acid (1 : 1). S. M. Jörgensen also obtained the salt as a by-product in preparing the oxalatotetramminonitrate. P. Pfeiffer and S. Basci agitated 100 grms. of green hexahydrated chromic chloride with 155 c.c. of pyridine ; and after adding 600 c.c. of water, allowed the mixture to stand for 7 to 10 hrs. Ten grams of the diaquodipyridinochloride were digested with 56 c.c. of 25 per cent. aq. ammonia at 45° to 48°. The deep reddish-violet soln. was treated with 68 c.c. of hydrochloric acid of sp. gr. 1·19. After standing 4 or 5 hrs. at ordinary temp., the prismatic crystals were separated from the mother-liquor. P. Pfeiffer obtained the same salt from the diaquotetramminochloride and hydrochloric acid. The deep red rhombic crystals are stable in air, but not if exposed to light. J. Peterson obtained a mol. wt. 262 by the f.p. method when the theoretical value is 251·5. Y. Shibata measured the absorption spectrum. A. Werner and A. Miolati found that a mol of the salt in $v$ litres of water had the mol. conductivity, $\mu$, at 25°,

| $v$ | 125 | 250 | 500 | 1000 | 2000 |
|---|---|---|---|---|---|
| $\mu$ | 212·6 | 231·6 | 245·6 | 261·2 | 274·8 |

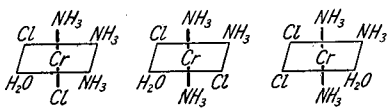
S. M. Jörgensen found that 100 grms. of water at 15° dissolve 6·4 grms. of the salt. The salt is decomposed when the soln. in water or alkali-lye is boiled ; hydrochloric acid precipitates the salt from the aq. soln. Oxalic acid precipitates from the soln., after standing some weeks, $Cr_2(C_2O_4)_3.6NH_3.3H_2O$ ; ammonium oxalate precipitates from the warm soln. chromic oxalate tetramminochloride and with potassium thiocyanate, P. Pfeiffer and M. Tilgner obtained chromic dithiocyanatotetramminothiocyanate ; with pyridine and sodium dithionate, P. Pfeiffer obtained chromic hydroxyaquotetramminodithionate. P. T. Cleve found that conc. sulphuric acid expels only two-thirds of the chlorine as hydrochloric acid ; and S. M. Jörgensen, that a nitric acid soln. of silver nitrate precipitates only two-thirds of the chlorine as silver chloride. There are also the sulphate, sulphide, nitrate, fluosilicate, bromide, iodide, oxalate, and chromate as well as complexes of the chloride with the mercuric and platinic chlorides of the aquochlorotetrammines. N. Bjerrum, R. F. Weinland and R. Krebs, R. F. Weinland and T. Schumann, and A. Recoura described **chromic chloropentaquodichloride,** $[Cr(H_2O)_5Cl]Cl_2$—*vide supra*. H. J. S. King found the conductivity, $\mu$ mhos, of a mol of the salt in $v$ litres, to be :

| $v$ | | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|
| $\mu$ | 0° | — | 134·8 | 142·1 | 146·8 | 151·2 |
| | 25° | 232·3 | 247·7 | 261·5 | 272·9 | 280·6 |

B. Klement gave 1·961 for the sp. gr., and 143·7 for the mol. vol. A. Werner and A. Miolati found that a soln. of a mol of the salt in 125, 250, 500, 1000, and 2000 litres of water at 25° had the mol. conductivity $\mu$=235·7, 257·5, 270·6, 280·1, and 283·6 respectively. P. T. Cleve prepared **chromic bromoaquotetramminodichloride,** $[Cr(NH_3)_4(H_2O)Br]Cl_2$, by the action of fuming hydrochloric acid on the bromide. S. M. Jörgensen prepared **chromic iodopentamminodichloride,** $[Cr(NH_3)_5I]Cl_2$, by the action of hydrochloric acid on the iodide. A. Werner and A. Miolati found that a mol of the salt in 125. 250, 500, 1000, and 2000 litres

of water at 25° had the mol. conductivity $\mu$=273·8, 292·5, 312·1, 326·9, and 342·8 respectively. The chloroplatinate was also obtained. F. Frowein, and E. H. Riesenfeld and F. Seeman prepared **chromic chlorodiaquotriamminodichloride,** $[Cr(NH_3)_3(H_2O)_2Cl]Cl_2$, by boiling an aq. soln. of one of the isomeric dichloroaquotriamminochlorides, and evaporating the liquid. The violet-red crystals form a red soln. with water. For the conductivity and the action of water, *vide supra*, the triaquotriamminotrichloride. A. Werner and J. von Halban prepared **chromic thiocyanatopentamminodichloride,** $[Cr(NH_3)_5(SCy)]Cl_2$.

F. Frowein, and E. H. Riesenfeld and F. Seemann prepared **chromic dichloroaquotriamminochloride,** $[Cr(NH_3)_3(H_2O)Cl_2]Cl$, by adding conc. hydrochloric acid to a soln. of chromium triamminotetroxide in well-cooled, dil. hydrochloric acid, and allowing the soln. to stand for some time. The reddish-violet, dichroic crystals form a blue soln. with water. If conc. hydrochloric acid is used instead of the dil. acid, a light green soln. is obtained, from which grey, needle-shaped crystals of a second modification of the above chloride separate, which is scarcely soluble in cold water, but dissolves in hot water to a red soln. A third modification is obtained by heating a hydrochloric acid soln. of the first chloride for some time at 60°. The soln. gradually becomes green in colour, and on evaporation in a desiccator, dark green crystals are obtained which dissolve in water to a green soln. None of these three chlorides readily loses water, which is therefore probably contained in the complex in all three salts. In all probability they are stereoisomerides:




At present it is impossible to say which formula corresponds with which isomeride. For the electrical conductivity, and hydrolysis, *vide supra*, the triaquotriamminotrichloride. F. Pintus prepared complexes with alcohol, $[Cr(C_2H_5.OH)_3Cl_3]$, and with thiourea, $[Cr(C_3SN_2H_4)_3Cl_3]$.

A. Werner and J. L. Klein, and A. Werner and J. V. Dubsky prepared **chromic dihydroxydiaquodiamminochloride,** $[Cr(OH)_2(H_2O)_2(NH_3)_2]Cl.H_2O$, by adding ammonia or pyridine to a conc. aq. soln. of the tetraquodiamminochloride; or by treating the bromide of the series with rubidium chloride. The crystals are lilac or reddish-violet. R. F. Weinland and co-workers, and A. Recoura also prepared the corresponding sulphate. P. Pfeiffer, and P. Pfeiffer and W. Osann prepared **chromic dihydroxydiaquodipyridinochloride,** $[CrPy_2(H_2O)_2(OH)_2]Cl$; and E. Weinmann, **chromic dihydroxydiaquoethylenediaminochloride,** $[Cr(H_2O)_2en(OH)_2]Cl$. A. Werner and J. L. Klein obtained **chromic dichlorodiaquodiamminochloride,** $[Cr(H_2O)_2(NH_3)_2Cl_2]Cl$, in pale green plates by the action of chlorine on a 25 per cent. aq. soln. of the tetrathiocyanatodiammine. The salt is soluble in water and with silver nitrate only one-third of the chlorine is precipitated. P. Pfeiffer and P. Koch, P. Pfeiffer and W. Stern, P. Pfeiffer and A. Trieschmann, and P. Pfeiffer prepared **chromic cis-dichlorobisethylenediaminochloride,** $[Cr\ en_2Cl_2]Cl.H_2O$, and a complex with antimonic and platinic chlorides; P. Pfeiffer, and P. Pfeiffer and P. Koch also prepared the **trans-salt**—anhydrous, monohydrate, hydrochloride, and chloroplatinate. A. Werner obtained **chromic dichloroaquotriamminochloride,** $[Cr(NH_3)_3(H_2O)Cl_2]Cl$, as well as the corresponding iodide, sulphate, and nitrate. P. Pfeiffer and M. Tapuach obtained **chromic dichlorodiaquodipyridinochloride,** $[CrPy_2(H_2O)_2Cl_2]Cl$, and a complex with pyridinium chloride, as well as the bromide, and nitrate. A. Werner and A. Gubser, P. Pfeiffer, N. Bjerrum, and R. F. Weinland and K. Feige discussed **chromic tetraquodichlorochloride,** $[Cr(H_2O)_4Cl_2]Cl$, previously described. P. Pfeiffer and M. Tilgner prepared **chromic dithiocyanatotetramminochloride,** $[Cr(NH_3)_4(SCy)]Cl$; P. Pfeiffer and P. Koch, **chromic cisdithiocyanatobisethylenediaminochloride,** $[Cr\ en_2(SCy)_2]Cl.H_2O$, and also the

**trans-salt ;** and P. Pfeiffer and S. Basci, **chromic oxalatotetramminochloride,** $[Cr(NH_3)_4(C_2O_4)]Cl$.

O. T. Christensen prepared **chromic hydroxydecamminopentachloride,** $[Cr_2(NH_3)_{10}(OH)]Cl_5.H_2O$, by treating the corresponding bromide with hydrochloric acid (1 : 1) ; and by the action of air on an ammoniacal soln. of ammonium chloride and chromic chloride. It was also obtained by P. Pfeiffer. J. Petersen gave for the average mol. wt. by the f.p. process 308, when the theoretical value is 469·5 ; and from the electrical conductivity process, the molecule furnishes 5·85 ions in dil. soln. A complex chloroplatinate, and a chloroiodide, were also prepared. S. M. Jörgensen prepared **chromic trihydroxyaquohexamminotrichloride,** $[Cr_2(OH)_3(H_2O)(NH_3)_6]Cl_3.H_2O$, as follows :

A soln. of chromous chloride, prepared by reducing a soln. of potassium dichromate with zinc and hydrochloric acid, is forced by hydrogen press. into a vessel containing a mixture of 700 grms. ammonium chloride, and 750 c.c. of aq. ammonia, sp. gr. 0·91. The vessel, entirely filled with this mixture, is closed by a stopper through which passes a delivery tube opening under water. The vessel is surrounded by cold water to moderate the reaction. The evolution of hydrogen takes place slowly, and ceases in about 24 hrs. The undissolved ammonium chloride is covered with trihydroxyaquohexamminotrichloride, a portion of which is also contained in the soln. from which it may be precipitated by alcohol ; the precipitate is washed with alcohol, and dried.

The salt was also prepared by P. Pfeiffer. J. Petersen found the mol. wt. 340 to 406 by the f.p. method—theoretical 364·5, and the electrical conductivity indicated that 3·76 ions per mol. are formed. The carmine-red prisms slowly lose a mol. of water over sulphuric acid ; at 100°, the salt gradually decomposes ; 100 parts of water at 18° dissolve 9·4 grms. of salt ; it is decomposed by boiling water ; boiling hydrochloric acid forms aquochlorotetramminochloride ; conc. hydrobromic acid precipitates the bromide ; solid potassium iodide, the iodide ; dil. sulphuric acid followed by alcohol precipitates the sulphate ; ammonium sulphate gives no precipitate ; hydrofluosilicic acid gives a red precipitate ; hydrochloroplatinic acid, forms acicular crystals ; hydrochloric acid, a reddish-brown precipitate ; potassium dichromate, an orange-yellow precipitate ; sodium pyrophosphate, a pale red precipitate soluble in excess ; sodium hydrophosphate, no precipitate ; ammonium thiocyanate, rhombic plates ; potassium ferrocyanide, lilac-coloured precipitate ; and potassium ferricyanide, a brown precipitate. P. Pfeiffer and W. Vorster prepared **chromic hexahydroxysexiesethylenediaminehexachloride,** $[Cr_4(OH)_6en_6]Cl_6.6H_2O$. M. Z. Jovitschitsch prepared **chromic dioxyhexammino-dichloride,** $Cr_4O_2(NH_3)_6Cl_2.10H_2O$, by dissolving the precipitate, obtained by adding ammonia to a chromic salt, in an excess of ammonia, and adding hydrochloric acid, and then alcohol. The violet-red precipitate is soluble in water, but only after standing a few hours will the soln. give a precipitate with silver nitrate. It is assumed that the salt is constituted :

$$\begin{matrix}(NH_3)_2=Cr.O.Cr=(NH_3)_2\\ \\ (NH_3)_2=Cr.O.Cr=Cl_2\end{matrix} + 10H_2O$$

A. Werner found that when chromium triamminotetroxide, $CrO_4(NH_3)_3$, is added to cold, conc. hydrochloric acid, a grey or bluish-grey precipitate is formed —probably a mixture of chromium triamminodichloroaquochloride and triammino-trichloride—and the filtrate, on standing for two days, deposits chromium triam-minotrichloride, $Cr(NH_3)_3Cl_3$, in dark blue crystals, tinged with green. The X-ray spectra of this salt and the corresponding pyridine salt $[Cr(Py)_3Cl_3]$, were studied by O. Stelling. According to A. Werner, the trichlorotriammine is almost insoluble in cold water ; it dissolves in hot water forming a blue soln. which furnishes a series of chromium **triamminodichloroaquo-salts** when treated with the appro-priate reagents.

Thus, **chromium triamminodichloroaquochloride,** $[Cr(H_2O)(NH_3)_3Cl_2]Cl$, is formed in brown-leaflets which give a blue soln. with water. The salt is also obtained by the action of conc. hydrochloric acid in the presence of glacial acetic acid on chromium triamminotetroxide. There are also **chromium triamminodichloroaquonitrate,** $[Cr(H_2O)(NH_3)_3Cl_2]NO_3$; **chromium triamminodichloroaquosulphate,** $[Cr(H_2O)(NH_3)_2Cl_2)_2SO_4$; **chromium triamminodichloroaquoiodide,** $[Cr(H_2O)(NH_3)_2Cl_2]I$; the basic iodide, **chromium triamminotriaquodihydroxyiodide,** $[Cr(H_2O)_3(NH_3)_3](OH)_2I$, and **chromium triamminotriaquotribromide,** $[Cr(H_2O)_3(NH_3)_3]Br_3$.

H. I. Schlesinger and R. K. Worner heated chromium chloropentamminochloride in air, hydrogen, carbon dioxide, or ammonia, and found that it furnishes chromium triamminotrichloride. Unless the temp. is carefully controlled, the reaction proceeds further. The black substance, reported by C. E. Ufer, and H. Schrötter, is formed. If the pentammine is heated in a stream of dry hydrogen chloride, a very rapid reaction occurs at about 270° with considerable evolution of heat and is accompanied by a marked colour change of the material from pink to green. If heating is discontinued at this point, the product washed with cold water to which a little hydrochloric acid has been added, and then dried with alcohol and ether, a very insoluble green substance, chromium trichlorotriammine is obtained. The triammine differs from that prepared by A. Werner. His compound is blue-green, dissolves fairly readily in warm water and especially easily in warm dil. hydrochloric acid to give a deep blue soln. of trichloroaquotriamminochloride; that of A. Werner is insoluble in hydrochloric acid or in water, but with the latter it slowly reacts to give a pink soln. which has since been shown to contain chromic diaquotetramminochloride. Here evidently is a case of isomerism of a type not frequently encountered, but whether it is stereoisomerism, possible according to A. Werner's theory, or is what is often called " polymerization isomerism," cannot be decided because of the insolubility of the compounds in question. Attempts to remove some of the three remaining molecules of ammonia from the co-ordination sphere show the firmness with which chromium retains the co-ordination number 6. When the triammine is heated to 175° in a stream of hydrogen chloride, ammonia is not withdrawn from the compound, but hydrogen chloride is quantitatively absorbed to give a reddish-purple very hygroscopic crystalline material which may be considered to be **ammonium chromic hexachloride,** $(NH_4)_3[CrCl_6]$. The substance is insoluble in all solvents except water, with which it reacts almost instantly to produce a deep green soln. presumably of hydrated chromic chloride. In favour of the argument that the ammonium compound is a salt of the complex ion $[CrCl_6]'''$, anhydrous chromic chloride, alone or when mixed with ammonium chloride, reacts with liquid ammonia to give a mixture of hexammine and chloropentammine chromic chlorides without the intermediate formation of a soln. What is called ammonium chromic hexachloride dissolves readily in liquid ammonia to give a green soln. which is transformed to the pentammine only after complete evaporation of the liquid. Anhydrous chromic chloride reacts exceedingly slowly with dry gaseous ammonia; the new compound reacts rapidly at ordinary temp. to give the pentammine. Double salts should possess a colour which is the summation of the colours of the constituent salts; the compound here prepared is decidedly different in colour from any known form of chromic chloride, the only coloured constituent. In this instance, then, chromium, rather than changing its co-ordination number as the result of removal of ammonia, takes up hydrogen chloride, and the ammonia, although removed from the co-ordination sphere, remains in the molecule. If the triamminotrichloride is treated with oxalic acid or an oxalate, **ammonium chromium triammino-oxalatochloride,** $(NH_4)_6[Cr_2(NH_3)_3(C_2O_4)Cl_{10}]$, is formed.

A. Johnsen [2] obtained no isomorphous mixtures of ammonium chloride and violet chromic chloride, but with green hexahydrated chromic chloride, the ammonium chloride crystals are coloured green. J. W. Retgers obtained solid soln. of both green and violet chromic chlorides from aq. soln. N. Larsson prepared **ammonium chromium tetrachloride,** $NH_4Cl.CrCl_3.6H_2O$, or $[CrCl(H_2O)_5]Cl_2.NH_4Cl.H_2O$, by

boiling a soln. of a mixture of chromic chloropentaquodichloride and ammonium chloride, and passing hydrogen chloride through the soln. cooled by a freezing mixture. G. Neumann prepared **ammonium chromic pentachloride,** $2NH_4Cl.CrCl_3.H_2O$, or $(NH_4)_2[CrCl_5(H_2O)]$, by adding ammonium chloride to a soln. of chromic chloride in 96–97 per cent. alcohol, and passing hydrogen chloride through the liquid heated on a water-bath with a reflux condenser. The violet, hygroscopic crystals of the *monohydrate* are probably rhombic. They are decomposed by water. A. Werner and A. Gubser represent this series of salts by $[Cr(H_2O)Cl_5](NH_4)_2$. R. F. Weinland and T. Schumann found that when hydrogen chloride is passed into an ice-cold soln. of equimolar proportions of green hexahydrated chromic chloride and ammonium chloride, green rectangular plates of the *hexahydrate* are formed. The salt is deliquescent, and turns red when warmed. A soln. of the salt acidified with nitric acid, and treated with silver nitrate deposits three-fifths of the chlorine as silver chloride. Hence the constitution of the salt is taken to be $(NH_4)_2[Cr(H_2O)_4Cl_2]Cl_3.2H_2O$. H. I. Schlesinger and R. K. Worner prepared **ammonium chromic hexachloride,** $(NH_4)_3CrCl_6$, in hygroscopic crystals, by heating chromic trichlorotriammine in hydrogen chloride at 175°. It reacts with ammonia to furnish chromic chloropentamminodichloride.

F. Ephraim and W. Ritter found that ammonia acts on potassium chromic aquopentachloride forming a greyish-violet mass of chromic hydroxypentammino-chloride. This dissolves in water, and nitric acid precipitates from the cherry-red soln., first chromium nitratopentamminodinitrate, and then chromic nitrataquo-tetramminodinitrate in a 27 per cent. yield; while hydrochloric acid precipitates from the cherry-red soln., the chloropentamminochloride in 40 per cent. yield. Similar results were obtained with the ammonium salt. F. Ephraim and W. Ritter suggest that ammonium hydroxypentachloride is formed as an intermediate compound. No evidence was obtained of the formation of ammines of the double salts.

A. Werner and A. Gubser [3] obtained **lithium chromium pentachloride,** $2LiCl.CrCl_3.5H_2O$, that is, $Li_2[Cr(H_2O)Cl_5].4H_2O$, as in the case of the ammonium salt, by passing hydrogen chloride into a soln. of 5 grms. of lithium chloride, and 17 grms. of hexahydrated chromic chloride. The red, hygroscopic powder is easily soluble in alcohol forming a green soln.; with water, the soln. is transiently red. At 0°, the salt gives no precipitate with silver nitrate when that salt is first added. N. Larsson found that **lithium chloropentaquodichloride,** $[CrCl(H_2O)_5]Cl_2.LiCl.nH_2O$, prepared as in the case of the ammonium salt, is very hygroscopic. J. J. Berzelius reported that when a soln. of sodium dichromate, hydrochloric acid, and alcohol is evaporated on the water-bath, a green mass of **sodium chromium tetrachloride,** $NaCrCl_4$, is formed, and it becomes violet on a sand-bath; N. Larsson obtained the salt **sodium chlorotetraquodichloride,** $[CrCl_2(H_2O)_4]Cl_2.NaCl.nH_2O$, as in the case of the sodium salt. J. J. Berzelius also prepared reddish-violet crystals of **potassium chromium tetrachloride,** $KCrCl_4$, in a similar manner; and found that the salt is decomposed when the aq. soln. is evaporated. L. Godefroy regarded this salt as a mixture of the pentachloride with chromic chloride. N. Larsson did not obtain $[CrCl(H_2O)_5]Cl_2.KCl.nH_2O$ by the method employed for the ammonium salt. L. Godefroy prepared **potassium chromium pentachloride,** $K_2CrCl_5.H_2O$, or $K_2[Cr(H_2O)Cl_5]$, by passing chlorine for 5 or 6 hrs. through a soln. of 300 grms. of powdered potassium dichromate and 700 grms. of alcohol; and G. Neumann obtained it by passing hydrogen chloride through a soln. of chromic and potassium chlorides in 96 to 97 per cent. alcohol warmed on a water-bath. The reddish, or violet-red crystalline powder is stable in air; it can be crystallized by heating it with 40 per cent. hydrochloric acid in a sealed tube at 120° to 130°. The crystals are probably rhombic; very hygroscopic; and are decomposed by water, forming potassium chloride and an oxychloride. For the action of ammonia, *vide supra*, the ammonium salt. J. J. Berzelius treated sodium chromium tetrachloride with alcohol, and obtained rose-red **sodium chromium hexachloride,** $Na_3CrCl_6$.

E. Zettnow, and J. J. Berzelius obtained **potassium chromium hexachloride,** $K_3CrCl_6$, in an analogous manner; and E. Frémy, found that when a mixture of potassium dichromate, mixed with charcoal, is heated in chlorine gas, chromic chloride sublimes, and the hexachloride remains. The salt is soluble in water, and at the same time is decomposed into its constituent chlorides. L. Godefroy said that the hexachloride is really a mixture of the pentachloride and potassium chloride.

N. Larsson prepared **rubidium chromium tetrachloride,** $RbCl.CrCl_3.5H_2O$, or $[CrCl(H_2O)_5]Cl_2.RbCl$, as in the case of the corresponding ammonium salt; and similarly with **cæsium chromium tetrachloride,** $CsCl.CrCl_3.5H_2O$, or $[CrCl(H_2O)_5]Cl_2.CsCl$. G. Neumann prepared **rubidium chromium pentachloride,** $Rb_2CrCl_5.H_2O$, or $Rb_2[Cr(H_2O)Cl_5]$, by the method employed for the potassium salt; and A. Werner and A. Gubser, by passing hydrogen chloride into a soln. of the constituent chlorides. The *monohydrate* furnishes reddish-violet crystals, sparingly soluble in cold water; and readily soluble in hot water forming a green soln. By working with the soln. at 0°, A. Werner and A. Gubser obtained the *octohydrate*, $[(ClRb.Cl)_2Cr(H_4O_2)_4]Cl$, in green, prismatic crystals, which lose water when confined over sulphuric acid, and deliquesce with decomposition in air. Only three-fifths of the chlorine is at first precipitated by silver nitrate. N. Larsson prepared the compound $[CrCl_2(H_4O_2]Cl.2RbCl$ from a soln. of chromic dichloro-aquochloride and rubidium chloride, cooled with a freezing mixture, and treated with hydrogen chloride. It is stable in air; alcohol extracts chromic chloride; at 85° it forms $Rb_2[CrCl_5(H_2O)]$. H. L. Wells and B. B. Boltwood prepared **cæsium chromium pentachloride,** $Cs_2CrCl_5.H_2O$, or $Cs_2Cr(H_2O)Cl_5$, by passing hydrogen chloride into a warm soln. of the component chlorides. The *monohydrate* forms violet crystals which are stable in air, and do not lose water at 160°. They dissolve slowly in water forming a green soln. which, on evaporation, yields crystals of the *tetrahydrate* which A. Werner and A. Gubser represent by the formula $(ClCsCl)_2Cr(H_2O)_4Cl$, because only three-fifths of the chlorine is at first precipitated by silver nitrate. This subject was discussed by R. F. Weinland and A. Koch. H. St. C. Deville obtained green crystals by fusing a mixture of chromic and sodium chlorides.

S. M. Jörgensen prepared **chromic hydroxydecamminotrichlorodichloraurate,** $[Cr_2(OH)(NH_3)_{10}]Cl_3(AuCl_4)_2$, in reddish-yellow needles by treating a soln. of $[Cr_2(OH)(NH_3)_{10}]Cl_5.H_2O$ with an aq. soln. of chlorauric acid. It loses its water of crystallization at 100°; and the salt is sparingly soluble in water. S. M. Jörgensen also prepared reddish-brown needles of **chromic trihydroxyaquohexamminochloro-dichloraurate,** $[Cr(OH)_3(H_2O)(NH_3)_6]Cl(AuCl_4)_2$, from $[Cr_2(OH)_3(H_2O)(NH_3)_6]Cl_3.H_2O$, in an analogous manner. It loses a mol of water over sulphuric acid.

G. Neumann obtained **beryllium chromium pentachloride,** $BeCrCl_5.H_2O$, by the method used in connection with the analogous potassium salt. He prepared **magnesium chromium pentachloride,** $MgCrCl_5.H_2O$, in a similar way. S. M. Jörgensen prepared the complex **chromic hexamminotrichloromercurichloride,** $[Cr(NH_3)_6]Cl_3.HgCl_2$. According to O. T. Christensen, when a conc. aq. soln. of aquopentamminotrichloride is treated with mercuric chloride, yellowish-red, sparingly soluble **chromic aquopentamminotrichlorotrismercurichloride,** $[Cr(NH_3)_5(H_2O)]Cl_3(HgCl_2)_3.H_2O$, is formed. He also prepared yellowish-red needles of **chromic nitritopentam-minodichlorobismercurichloride,** $[Cr(NH_3)_5(NO_2)]Cl_2(HgCl_2)_2$. S. M. Jörgensen similarly obtained **chromic chloropentamminodichlorotrismercurichloride,** $[Cr(NH_3)_5Cl]Cl_2(HgCl_2)_3$, in rose-red needles; and P. T. Cleve, **chromic aquochloro-tetramminodichlorotrismercurichloride,** $[Cr(NH_3)_4(H_2O)Cl]Cl_2(HgCl_2)_3$, in rose-red plates. G. Neumann prepared **thallous chromium hexachloride,** $Tl_3CrCl_3$, in hygroscopic, violet crystals, by the process used for potassium chromium pentachloride. R. F. Weinland and E. Gussmann prepared **chromic hexacetatohydroxy-aquotripyridinochlorostannate,** $[Cr_3(CH_3COO)_6Py_3(H_2O)(HO)]SnCl_6.7H_2O$, in pale grey needle-like crystals, from the acetate of the series and sodium chlorostannate.

P. Pfeiffer and M. Tapuach prepared **chromic cis-dichlorobisethylenediamino-chloroantimonate,** $[Cr\ en_2Cl_2]SbCl_6$, from the chloride of the series and a hydrochloric acid soln. of antimony pentachloride.

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## § 26. Chromium Bromides and Oxybromides

A. Moberg [1] observed the formation of a dark green mixture when chromous chloride is treated with potassium bromide ; but the product was not examined. F. Wöhler, M. Bauck, and H. Moissan observed that **chromous bromide,** or **chromium dibromide,** $CrBr_2$, is formed by passing hydrogen over heated chromic bromide ; and H. Moissan also obtained it by the action of dry hydrogen bromide on chromium at a high temp. ; and by passing a mixture of bromine vapour and nitrogen over an excess of chromium at a red-heat. An aq. soln. of chromous bromide is formed by reducing a soln. of chromic bromide with zinc and hydrobromic acid. W. Biltz and E. Birk gave 4·356 for the sp. gr. at 25°/4°. According to A. Moberg, H. Moissan, F. Wöhler, and M. Bauck, white, crystalline chromous bromide readily fuses to a yellow liquid ; it forms a blue soln. with water, and the soln. quickly absorbs oxygen. The salt rapidly deliquesces in air forming green chromic bromide. The salt is soluble in alcohol. The presence of a trace of chromous bromide will bring anhydrous chromic chloride, bromide, or iodide into soln.—*vide supra*, chromic chloride. W. Biltz and E. Birk gave 1·714 for the sp. gr. of **chromous hexamminobromide,** $CrBr_2.6NH_3$, at 25°/4°. W. Traube and W. Passarge found that with hydrazine, chromous bromide forms **chromous dihydrazinobromide,** $CrBr_2.2N_2H_4$.

A. J. Balard obtained a soln. of **chromic bromide,** $CrBr_3$, by the action of bromine-water on the green hydrated chromic oxide, and the filtrate, when concentrated by evaporation, deposits green crystals—presumably the hydrate (*q.v.*). C. Löwig found that if lead chromate be boiled with hydrobromic acid, a dark green soln. is obtained ; he could not get the conc. soln. to crystallize, and he obtained a yellowish-red powder on evaporation. J. J. Berzelius used silver chromate in place of the lead salt. J. B. Berthemot obtained a soln. of the salt by the action of hydrobromic acid on chromic acid, in which case bromine is evolved ; he found that the green aq. soln. of chromic bromide turns brown on evaporation, and crystallizes with difficulty ; if further evaporated, the residue evolves hydrobromic acid. He prepared the anhydrous bromide by the action of bromine vapour on heated chromium—the combination is attended incandescence ; H. Moissan obtained it in an analogous way. F. Wöhler, and M. Bauck prepared it, as in the analogous case of chromic chloride, by the action of bromine vapour on a heated mixture of chromic oxide and carbon. F. Bourion prepared the bromide by passing the vapour of sulphur monochloride in a slow current of hydrogen bromide over chromic oxide at 135°, and finishing off with hydrogen bromide alone. The black plates or scaly crystals of chromic bromide appear olive-green by reflected light, and there is a pleochroic red colour as well. The powder is yellowish-green. W. Biltz and E. Birk gave 4·250 for the sp. gr. at 25°/4°. According to F. Wöhler, M. Bauck, and F. Bourion, when the anhydrous tribromide is heated in air, chromic oxide is formed ; in hydrogen, chromous bromide. The anhydrous salt appears to be insoluble in water, but it forms a green aq. soln. if a trace of chromous bromide be present. Chromic bromide deliquesces when exposed on tin-foil forming a green soln. The salt is soluble in boiling water ; alkali-lye decomposes it more easily than is the case with the chloride.

L. Varenne reported crystals of the *octohydrate*, $CrBr_3.8H_2O$, to be formed by treating a cold, conc. soln. of potassium or ammonium trichromate with dil. hydrobromic acid, and allowing the liquor to stand at 0°. The violet crystals are a combination of the cube and octahedron. The salt loses water at 110° and becomes green ; at 200°, in air, it forms an oxybromide, and finally chromic oxide. A. Werner

and A. Gubser could not confirm these results. Chromic bromide furnishes a *hexahydrate* which occurs in two isomeric forms—green, and violet. The facts in connection with the isomeric hexahydrates of chromic chloride are applicable to the bromide. The **green hexahydrate** is considered to be **chromic dibromohexaquobromide,** $[(H_2O.Br)_2Cr(H_2O)_4]Br$, or $[Cr(H_2O)_4Br_2]Br.2H_2O$. A. Recoura obtained it by evaporating a sat. soln. of chromic oxide with a large excess of hydrobromic acid; and A. Werner and A. Gubser recommended passing hydrogen bromide over the evaporating soln. The green, hygroscopic crystals are acicular or tabular, which have, according to R. F. Weinland and A. Koch, the same optical properties as the green chloride, but it is rather stronger yellow tinge. A. Byk and H. Jaffe studied the violet and ultra-violet absorption spectrum of aq. soln. C. S. Garrett examined the effect of the chlorides of lithium, potassium, calcium, zinc, mercury, and aluminium on the mol. extinction of soln. of chromic bromide after standing 3 days, and $3\frac{1}{2}$ months. The results are said to make it appear as if the water mols. play an initial part in changing the complex to the simple configuration, and that following this a second reaction sets in tending again to the formation of complexes owing to the presence of the colourless haloids in the soln. When, however, the colourless haloids have decidedly dehydrating properties, the hydration on dilution is initially inhibited, although the final point reached, when an excess of water mols. is present, is independent of the hygroscopic properties of the colourless haloid. N. Bjerrum found that the electrical conductivity of a freshly prepared soln. of a mol of the salt in 625 litres of water is 70 to 80 mhos at 0°, and 265·1 mhos at 25°. It forms only two ions, $[Cr(OH)_4Br_2]'$ and $Br'$. This is in agreement with the observation that only one-third of the bromine is at once precipitated on adding silver nitrate. E. Rosenbohm gave for the magnetic susceptibility, $13{\cdot}96\times10^{-6}$ mass units. A. Werner and A. Gubser found that the transformation of the green into the violet soln. is faster than is the case with the chloride. A. Recoura found that the salt is very soluble in water, and that the heat of soln. is 0·68 Cal. The aq. soln. reacts acid, and has a sweet taste. The salt is easily soluble in alcohol, and insoluble in ether. I. Koppel described a brown alcoholate, $CrBr_3.3C_2H_5OH$, or $[Cr(C_2H_5OH)_3Br_3]$, analogous to the red chloride; and P. Pfeiffer, the complex with pyridinium chloride, $[Cr(H_2O)_3Br_3].2PyHBr$. A. Werner and A. Gubser found that it is soluble in acetone, and precipitated by ether. N. Bjerrum said that it is soluble in fuming hydrobromic acid, but insoluble in a mixture of ether and this fuming acid. J. M. Ordway found that the aq. soln. of a mol of the salt dissolves 2 mols of the hydrated oxide.

The blue, greyish-blue, or **violet hexahydrate** is symbolized, as in the case of the corresponding hydrate of chromic chloride, by $[Cr(H_2O)_6]Br_3$, that is, **chromic hexaquotribromide.** A. Recoura prepared it by passing hydrogen bromide into a boiling, conc. soln. of the green hexahydrate. The soln. becomes brown, and as it cools, it deposits the violet salt. A. Werner and A. Gubser, and R. F. Weinland and A. Koch dissolved the product in a little water, and again passed hydrogen bromide into the soln. cooled below zero. G. O. Higley obtained the violet hexahydrate by saturating with hydrogen bromide a soln. of 5 grms. of the violet sulphate in 20 c.c. of water at 10°. The greyish-blue or violet powder was found by R. F. Weinland and A. Koch to have the same crystal form as the corresponding chloride. The violet and ultra-violet absorption spectra of the soln. were examined by A. Byk and H. Jaffe. The crystals are hygroscopic, and have a sweet taste. A. Recoura found that it dissolves in water with the development of 14·35 Cals. At 100°, it passes into the green isomer, and the heat of transformation from the green solid to the blue isomer is −2·17 Cals. The heat of the reaction $CrBr_{3\,violet\ soln.}+3NaOH_{aq.}=3NaCl_{soln.}+Cr(OH)_3$ is 21·6 Cals. The phenomena associated with the conversion of the green into the blue soln. resemble those in the analogous conversion with the chloride (*q.v.*). The rate of conversion is much greater with the bromide than with the chloride. Thus, the molar conductivity, $\mu$ mhos, of a 0·008*M*-soln., with time is:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1° | Time | 0 | 2 | 8 | 25 | 70 | 110 | 160 min. |
| | $\mu$ . | 76·7 | 77·2 | 94·5 | 111·1 | 125·8 | 136·3 | 156·1 mhos. |
| 25° | Time | 0 | 2 | 5 | 10 | 20 | 30 | 50 min. |
| | $\mu$ . | 265·1 | 288·5 | 300·7 | 319·9 | 322·4 | 325·1 | 325·1 mhos. |

The transformation to a state of equilibrium is thus completed in 30 min. at 25°, but not in 160 min. at 1°. A. Recoura gave 11·5 Cals. for the complete transformation of a mol of the green salt in soln. In the cold in dil. soln. the violet form is favoured, while an increase of temp., concentration, or the presence of hydrobromic acid favours the green. Unlike the case of the chlorides, N. Bjerrum found that the violet isomer occupies the greater vol. A. Recoura noticed that in concentrating a violet soln. of the bromide, the violet isomer first separates out, while with a violet soln. of the chloride, the dark green form appears. A. Werner and A. Gubser found the mol. conductivity of the violet soln. with a mol of the salt in $v$ litres at 0° is $\mu$=173 mhos when $v$=125 at 0°, and at 25°, when $v$=125, 250, 500, and 1000, $\mu$=329·5, 360·3, 391·2, and 431·6 mhos respectively. The results indicate that a mol. of the salt forms four ions when dissolved in water, *viz.*, $[Cr(H_2O)_6]^{\cdots}$ and $3Br'$, and is in agreement with the fact that all the bromine is at once precipitated by silver nitrate. The results are summarized by the formula $[Cr(H_2O)_6]Br_3$. A. Recoura said that the salt is insoluble in alcohol, A. Werner and A. Gubser said that it is soluble in acetone, and insoluble in ether. The hydrated chromic hydroxide precipitated by alkali-lye dissolves in acid forming the violet soln. E. Hein and co-workers studied some complexes with organic radicles.

S. M. Jörgensen [2] found that when a soln. of the hexamminonitrate is treated with conc. hydrobromic acid, and the precipitate is washed with dil. hydrobromic acid and then with alcohol, there is formed orange-yellow, rhombic plates of **chromic hexamminobromide,** $[Cr(NH_3)_6]Br_3$. F. Pintus also prepared this salt. W. Biltz and E. Birk found the sp. gr. to be 2·151 at 25°/4°, and the mol. vol. 183·2. J. Petersen, and P. Pfeiffer found the mol. wt. by the cryoscopic method and the mol. conductivity corresponds with the formation of four ions. H. J. S. King gave for the conductivity, $\mu$ mhos, of a mol of the salt in $v$ litres at 25°, $\mu$=355·5 for $v$=64 ; $\mu$=391 for $v$=391·1 ; and $\mu$=423·3 for $v$=256. It also forms a complex bromoplatinate. F. Ephraim and W. Ritter found that no ammonia is absorbed by the hexamminotribromide at room temp., but when cooled by a freezing mixture ammonia gas is absorbed, and the decomposition curve of the ammine of the hexamminotribromide is that represented by Fig. 78, and it shows that a triammine and monammine are formed. P. Pfeiffer, and F. Pintus obtained the corresponding **chromic trisethylenediaminotribromide,** $[Cr\ en_3]Br_3.nH_2O$ ; P. Pfeiffer and H. Pietsch, **chromic bisethylenediaminopropylenediaminotribromide,** $[Cr\ en_2pn]Br_3.3H_2O$ ; and F. Pintus, **chromium tripyridinotribromide,** $[CrPy_3]Br_3$. H. Farl studied the complexes with pyridine and chromic dichloroethylate. A. Benrath found that in the presence of hydrobromic acid, $[Cr(NH_3)_5Br]Br_2$, and $[Cr(NH_3)_5(H_2O)]Br_3$ are formed. O. T. Christensen prepared **chromic aquopentamminotribromide,** $[Cr(NH_3)_5(H_2O)]Br_3$, from an aq. soln. of the hydroxide and hydrobromic acid (1 : 3). The yellow crystalline powder is soluble in water, and loses a mol. of water at 110°. H. J. S. King also prepared this salt. F. Ephraim and W. Ritter found that the salt absorbs ammonia in the cold, and that the decomposition curve of the product shows the existence of an octammine and a tetrammine. A. Benrath found that the stable phase in the presence of hydrobromic acid is $[Cr(NH_3)_5Br]Br_2$. P. Pfeiffer treated chromic hydroxyaquotetramminodithionate with conc. hydrobromic acid, and obtained a brick-red crystalline powder of **chromic diaquotetramminotribromide,** $[Cr(NH_3)_4(H_2O)_2]Br_3$.

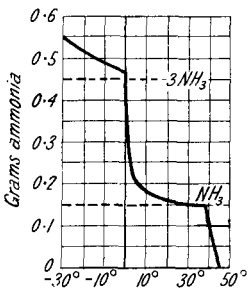


FIG. 78.—Dissociation of the Ammine of Chromic Hexamminotribromide.

P. Pfeiffer and R. Stern prepared **chromic cis-diaquobisethylenediaminotribromide,** $[Cr\ en_2(H_2O)_2]Br_3.2H_2O$; and P. Pfeiffer and R. Prade obtained the **trans-salt.** A. Werner prepared **chromic triaquotriamminotribromide,** $[Cr(H_2O)_3(NH_3)_3]Br_3$, by the action of hydrobromic acid on the hydroxyaquotriamminoiodide; and A. Werner and J. L. Klein, **chromic tetraquodiamminotribromide,** $[Cr(NH_3)_2(H_2O)_4]Br_3$, by the action of hydrobromic acid on the dihydroxydiaquodiamminobromide; P. Pfeiffer, and P. Pfeiffer and M. Tapuach also obtained **chromic tetraquodipyridinotribromide,** $[CrPy_2(H_2O)_4]Br_3.2H_2O$.

H. J. S. King prepared **chromic hydroxypentamminobromide,** $[Cr(NH_3)_5(OH)]Cl_2.\frac{1}{2}H_2O$, as in the case of the corresponding chloride. F. Ephraim and W. Ritter found that the salt absorbs ammonia in the cold but the decomposition curve shows no signs of the formation of a definite ammine. P. Pfeiffer prepared **chromic hydroxyaquotetramminodibromide,** $[Cr(NH_3)_4(H_2O)(HO)]Br_2$, by adding pyridine to a conc. soln. of the diaquotetramminodibromide. P. Pfeiffer, and P. Pfeiffer and R. Stern prepared **chromic cis-hydroxyaquobisethylenediaminodibromide,** $[Cr\ en_2(H_2O)(HO)]Br_2.H_2O$, or $[Cr\ en_2(H_4O_2)(HO)]Br_2$; and P. Pfeiffer and R. Prade prepared the **trans-salt.** O. T. Christensen obtained **chromic nitritopentamminodibromide,** $[Cr(NH_3)_5(NO_2)]Br_2$, by the action of potassium or ammonium bromide on the chloride of the series. S. M. Jörgensen obtained carmine-red octahedral crystals of **chromic chloropentamminodibromide,** $[Cr(NH_3)_5Cl]Br_2$, by the action of hydrobromic acid on the chloride of the series; he also obtained a complex with mercuric bromide. R. Klement gave 2·129 for the sp. gr., and 156·2 for the mol. vol. of the dibromide. S. M. Jörgensen, and P. T. Cleve prepared **chromic chloroaquotetramminodibromide,** $[Cr(NH_3)_4(H_2O)Cl]Br_2$, by the action of hydrobromic acid on the chloride of the series. R. Werner and A. Miolati found the electrical conductivity of a mol of the salt in $v$ litres of water at 25° to be:

| $v$ | . . | 125 | 250 | 500 | 1000 | 2000 |
|---|---|---|---|---|---|---|
| $\mu$ | . . | 220·7 | 236·8 | 251·1 | 264·8 | 290·9 |

S. M. Jörgensen, and O. T. Christensen prepared **chromic bromopentamminodibromide,** $[Cr(NH_3)_5Br]Br_2$, by the action of hydrobromic acid on the product of the action of silver oxide on the chloropentamminodichloride. R. Klement gave 2·382 for the sp. gr., and 158·2 for the mol. vol. It forms a complex chloroplatinate. The nitrate, chloride, and chromate of the series $Cr(NH_3)_5BrX_2$ were also obtained. F. Ephraim and W. Ritter found that the salt absorbs no ammonia. A. Benrath found that the salt is stable in the presence of hydrobromic acid. R. Klement gave 1·961 for the sp. gr. and 146·9 for the mol. vol. of **chromic bromopentamminodichloride,** $[Cr(NH_3)_5Br]Cl_2$. H. Freundlich and R. Bartels studied the hydrolysis of the salt $[Cr(NH_3)_5Br]^{\cdot\cdot} + H_2O = Br' + [Cr(NH_3)_5(H_2O)]^{\cdot\cdot\cdot}$. P. T. Cleve, and P. Pfeiffer and S. Basci prepared **chromic bromoaquotetramminodibromide,** $[Cr(NH_3)_4(H_2O)Br]Br_2$, by the action of hydrobromic acid on an ammoniacal soln. of ammonium bromide and chromic hydroxide. The chloride and sulphate of the series were also prepared. A. Werner obtained **chromic bromodiaquotriamminodichloride,** $[Cr(NH_3)_3(H_2O)_2Br]Cl_2$; and also **chromic bromodiaquotriamminodibromide,** $[Cr(NH_3)_3(H_2O)_2Br]Br_2$; as well as the corresponding sulphate. P. Pfeiffer and R. Stern, and P. Pfeiffer and T. G. Lando obtained **chromic bromoaquobisethylenediaminodibromide,** $[Cr\ en_2(H_2O)Br]Br_2.H_2O$. A. Werner and J. von Halban prepared dark orange crystals of **chromic thiocyanatopentamminodibromide,** $[Cr(NH_3)_5(SCy)]Br_2$; H. I. Schlesinger and D. N. Rickles also prepared **chromium cis-dibromotetramminochloride,** $[Cr(NH_3)_4Br_2]Cl$, by the action of boiling hydrobromic acid on **chromium triamminochloroxalate,** $[Cr(NH_3)_3Cl(C_2O_4)]$. They also prepared the corresponding **chromium cis-dibromotetramminobromide,** $[Cr(NH_3)_4Br_2]Br$, **chromium cis-dibromotetramminoiodide,** $[Cr(NH_3)_4Br_2]I$, etc. They also prepared **chromium trans-dibromotetramminobromide,** $[Co(NH_3)_3Br_2]Br$, by the action of hot hydro-

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bromic acid on chromium triamminobromide. A. Werner and J. L. Klein obtained lilac-coloured crystals of **chromic dihydroxydiaquodiamminobromide,** $[Cr(NH_3)_2(H_2O)_2(OH)_2]Br.H_2O$, by the action of pyridine on a soln. of dibromodiaquodiamminobromide; and E. Weinmann, on chromic dihydroxydiaquoethylenediaminoiodide, $[Cr(H_2O)_2\ en(OH)_2]I$. P. Pfeiffer and W. Osann prepared **chromic dihydroxydiaquodipyridinobromide,** $[CrPy_2(H_2O)_2(OH)_2]Br$. P. Pfeiffer and T. G. Lando, and A. Werner prepared **chromic cis-dichlorobisethylenediaminobromide,** $[Cr\ en_2Cl_2]Br.H_2O$, A. Werner, and P. Pfeiffer and P. Koch obtained the **trans-salt**; P. Pfeiffer and M. Tapuach, **chromic dichlorodiaquodipyridinobromide,** $[CrPy_2(H_2O)_2Cl_2]Br.3H_2O$; P. Pfeiffer and A. Trieschmann, **chromic cis-dibromobisethylenediaminobromide,** $[Cr\ en_2Br_2]Br.H_2O$, as well as the corresponding iodide, and dithionate. The **trans-salt** was also obtained as well as the corresponding iodide, nitrate, iodide, and thiocyanate. E. H. Riesenfeld and F. Seemann, and S. Guralsky prepared **chromic dibromoaquotriamminobromide,** $[Cr(NH_3)_3(H_2O)Br_2]Br$, as well as the corresponding iodide, sulphate, nitrate, and thiocyanate. Y. Shibata measured the absorption spectrum of the bromide. N. Bjerrum found that **chromic dibromotetraquochloride,** $[Cr(H_2O)_4Br_2]Cl.2H_2O$, is precipitated when a cold soln. of chromic dibromotetraquobromide in dil. hydrochloric acid is sat. with hydrogen chloride. Its constitution is deduced from its method of formation, its colour, which resembles that of the dibromobromide, and from the ease with which the halogen in the metallic complex is brought into the ionized state by soln. in water or nitric acid. He also prepared **chromic dichlorotetraquobromide,** $[Cr(H_2O)_4Cl_2]Br$, in a similar manner, as an unstable, green, crystalline powder; titration by silver nitrate shows that only one halogen atom is in the ionized state in soln. A. Werner and J. V. Dubsky, and A. Werner and J. L. Klein prepared **chromic dibromodiaquodiamminobromide,** $[Cr(NH_3)_2(H_2O)_2Br_2]Br$; and P. Pfeiffer and M. Tapuach, **chromic dibromodiaquodipyridinobromide,** $[CrPy_2(H_2O)_2Br_2]Br.4H_2O$, as well as the corresponding nitrate, and iodide. P. Pfeiffer and M. Tilgner obtained **chromic dithiocyanatotetramminobromide,** $[Cr(NH_3)_4(SCy)_2]Br$; P. Pfeiffer and P. Koch, **chromic dithiocyanatobisethylenediaminobromide,** $[Cr\ en_2(SCy)_2]Br.H_2O$, and P. Pfeiffer obtained the trans-salt; P. Pfeiffer, **chromic oxalatotetramminobromide,** $[Cr(NH_4)_4(C_2O_4)]Br.\frac{1}{2}H_2O$; H. Schwarz, P. Pfeiffer and A. Trieschmann, **chromic oxalatobisethylenediaminobromide,** $[Cr\ en_2(C_2O_4)]Br.H_2O$.

H. I. Schlesinger and D. N. Rickles prepared **chromic triamminotribromide,** $[Cr(NH_3)_3Br_3]$, **chromic triamminochlorodibromide,** $[Cr(NH_3)_3Br_2Cl]$, and **chromic triamminodichlorobromide,** $[Cr(NH_3)_3BrCl_2]$, as in the case of chromic triamminotrichloride, by the thermal decomposition of the corresponding pentammines at 175°. The corresponding iodo-, nitrato-, and nitrito-salts could not be similarly obtained.

S. M. Jörgensen, J. Petersen, and P. Pfeiffer prepared **chromium hydroxydecamminopentabromide,** $[Cr_2(OH)(NH_3)_{10}]Br_5.H_2O$, and its bromoplatinate; as well as **chromic hydroxydecamminohydroxytetrabromide,** $[Cr_2(OH)(NH_3)_{10}]Br_4(OH).H_2O$. S. M. Jörgensen described **chromic hydroxydecamminotetrabromide,** $[Cr_2(OH)(NH_3)_{10}]Br_4.2H_2O$; P. Pfeiffer and R. Stern, **chromic dihydroxybisethylenediaminotetrabromide,** $[Cr(OH)_2en_2]Br_4.2\frac{1}{2}H_2O$; S. M. Jörgensen, **chromic trihydroxyaquohexamminotribromide,** $[Cr_4(OH)_3(H_2O)(NH_3)_6]Br_3.H_2O$; P. Pfeiffer and W. Vorster, **chromic hexaquosexiesethylenediaminohexabromide,** $[Cr_4(OH)\ en_6]Br_6.4H_2O$.

A. Werner and A. Gubser prepared **rubidium chromium bromide,** $2RbBr.CrBr_3.H_2O$, or $Rb[CrBr_5(H_2O)]$, from a soln. of 3 grms. of rubidium bromide, 8 grms. of green chromic bromide, and 10 grms. of water. The brownish-violet crystals are soluble in water. S. M. Jörgensen prepared **chromic chloropentamminodibromomercuribromide,** $[Cr(NH_3)_5Cl]Br_2.2\frac{1}{4}HgBr_2$; and P. Pfeiffer, **chromic dibromobisethylenediaminobromomercuribromide,** $[Cr\ en_2Br_2]Br.HgBr_2$.

H. Rose [3] heated a mixture of potassium dichromate and bromide with sul-

phuric acid, and found that bromine distils over without a trace of chromium. No signs of a **chromyl bromide,** $CrO_2Br_2$, analogous with the corresponding chloride was obtained. S. G. Rawson also failed to prepare the compound by H. Rose's method, and also by heating calcium bromide and chromyl chloride in sealed tubes at varying temp. and varying periods of time. H. S. Fry found that a soln. of acetyl bromide in carbon tetrachloride, to which a few drops of acetic acid are added, produces an intense permanganate-red coloration, which rapidly changes to reddish-brown. The latter colour is due to bromine, and the former to an unstable chromyl bromide. The production of the permanganate-red colour is recommended as a test for traces of chromium, and is capable of detecting 0·01 mg. per 1 c.c. of solvent.

A. Ditte prepared **potassium bromochromate,** $KCrO_3Br$, from a mixed soln. of chromic acid and potassium bromide evaporated in the cold in vacuo. J. Heintze obtained it from a soln. of potassium chromate and fuming hydrobromic acid. The red crystals lose bromine in the desiccator; water decomposes the salt into potassium dichromate and hydrobromic acid; and with nitrogen peroxide, nitroxyl bromide is formed.

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## § 27. Chromium Iodides and Oxyiodides

A. Moberg [1] observed that a soln. of chromous chloride does not give a precipitate with potassium iodide, but the soln. acquires a reddish-brown colour. H. Moissan prepared **chromous iodide**, or **chromium diiodide**, $CrI_2$, by heating chromic iodide in hydrogen. The greyish-white product forms a blue soln. with water; and this, on exposure, becomes green owing to the absorption of oxygen. The presence of this salt in water can induce the dissolution of the insoluble forms of the anhydrous chromic halides. W. Biltz and E. Birk gave 5·196 for the sp. gr. of **chromous hexamminodiiodide**, $CrI_2.6NH_3$.

J. Inglis observed that when a soln. of potassium dichromate is treated with an excess of conc. hydriodic acid, a dense black precipitate of iodine separates out. J. M. Ordway said that a soln. of a mol of hydrogen iodide dissolves 3 mols of chromic oxide. P. Guyot found that by heating the mixture of potassium dichromate and hydriodic acid, there remains after the expulsion of the iodine, a mixture of potassium iodide, and what was said to be **chromic iodide**, or **chromium triiodide**, $CrI_3$. H. Moissan obtained red crystals of anhydrous chromic iodide by the action of iodine vapour carried by a current of nitrogen over red-hot chromium; R. Hanslian observed no reaction at the b.p. of iodine. According to G. O. Higley, the violet *enneahydrate*, $CrI_3.9H_2O$, or $[Cr(H_2O)_3(H_4O_2)_3]$, is formed by passing hydrogen iodide into 30 c.c. of water in which 12·3 grms. of barium carbonate are suspended and then adding 14·5 grms. of violet chromic sulphate, and sat. the filtrate at 10° with hydrogen iodide. The dark violet or black crystals yield an olive-green powder. The salt decomposes on keeping with the evolution of hydrogen iodide; it is very hygroscopic; and it is soluble in alcohol, and in acetone, but insoluble in chloroform. W. Biltz and E. Birk gave 4·915 for the sp. gr. at 25°/4°.

S. M. Jörgensen [2] treated a soln. of chromic hexamminonitrate with a soln. of potassium iodide, and obtained **chromic hexamminotriiodide**, $[Cr(NH_3)_6]I_3$. The yellow, rhombic plates are isomorphous with the bromide. W. Biltz and E. Birk gave 2·425 for the sp. gr. at 25°/4°; and 220·6 for the mol. vol. E. Rosenbohm gave $10·53\times10^{-6}$ mass units for the magnetic susceptibility. A. Benrath found that in the presence of hydriodic acid, $[Cr(NH_3)_5I]I_2$, and $[Cr(NH_3)_5(H_2O)]I_3$ are formed. P. Pfeiffer, and P. Pfeiffer and M. Tilgner prepared **chromic trisethylenediaminotriiodide**, $[Cr\ en_3]I_3.H_2O$; P. Pfeiffer and H. Pietsch, **chromic bisethylenediaminopropylenediaminotriiodide**, $[Cr\ en_2pn]I_3.2H_2O$; and P. Pfeiffer and M. Haimann, **chromic trispropylenediaminotriiodide**, $[Cr\ pn_3]I_3.H_2O$. O. T. Christensen obtained a yellow crystalline powder of **chromic aquopentamminotriiodide**, $[Cr(NH_3)_5(H_2O)]I_3$, by the action of hydriodic acid on a soln. of the corresponding hydroxide. H. J. S. King also prepared this salt.

H. J. S. King prepared **chromic hydroxypentamminodiiodide**, $[Cr(NH_3)_5(OH)]I_2.\frac{1}{2}H_2O$, as in the case of the chloride. An addition product with potassium iodide was also obtained. P. Pfeiffer and R. Stern obtained **chromic cis-hydroxyaquobisethylenediaminodiiodide**, $[Cr\ en_2(H_2O)(OH)]I_2$; and P. Pfeiffer and R. Prade, the **trans-salt**. O. T. Christensen prepared red, octahedral crystals of **chromic nitritopentamminodiiodide**, $[Cr(NH_3)_5(NO_2)]I_2$; and A. Werner and J. von Halban, **chromic**

**nitratopentamminodiiodide,** $[Cr(NH_3)_5(NO_3)]I_2$. S. M. Jörgensen obtained lilac plates of **chromic chloropentamminodiiodide,** $[Cr(NH_3)_5Cl]I_2$, associated with one and two mols. of mercuric iodide. P. T. Cleve prepared garnet-red, rhombic prisms of **chromic chloroaquotetramminodiiodide,** $[Cr(NH_3)_4(H_2O)Cl]I_2$. S. M. Jörgensen obtained bluish-violet, octahedral crystals of **chromic iodopentamminodiiodide,** $[Cr(NH_3)_5I]I_2$, as well as the corresponding chloride, and nitrate. H. Freundlich and R. Bartels studied the hydrolysis of the salt: $[Cr(NH_3)_5I]^{\cdot\cdot} + H_2O = I' + [Cr(NH_3)_5(H_2O)]^{\cdot\cdot\cdot}$. P. T. Cleve prepared **chromic iodoaquotetramminodiiodide,** $[Cr(NH_3)_4(H_2O)I]I_2$, *in* rose-red octahedra; A. Werner and J. V. Dubsky, **chromic dihydroxydiaquodiamminoiodide,** $[Cr(NH_3)_2(H_2O)_2(OH)_2]I$; E. Weinmann, **chromic dihydroxydiaquoethylenediaminoiodide,** $[Cr(H_2O)_2\ en(OH_2)]I$; P. Pfeiffer and W. Osann, **chromic dihydroxydiaquodipyridinoiodide,** $[CrPy_2(H_2O)_2(OH)_2]I$; P. Pfeiffer and T. G. Lando, P. Pfeiffer and P. Koch, and P. Pfeiffer and A. Trieschmann, **chromic cis-dichlorobisethylenediaminoiodide,** $[Cr\ en_2Cl_2]I$, and also the trans-salt; E. Rosenbohm, **chromic dichlorotetramminoiodide,** $[Cr(NH_3)_4Cl_2]I$, with the magnetic susceptibility $19{\cdot}74 \times 10^{-6}$ mass units; A. Werner, **chromic dichloroaquotriamminoiodide,** $[Cr(NH_3)_3(H_2O)Cl_2]I$; S. Guralsky, and A. Werner, **chromic dibromoaquotriamminoiodide,** $[Cr(NH_3)_3(H_2O)Br_2]I$; P. Pfeiffer, **chromic cis-dibromobisethylenediaminoiodide** $[Cr\ en_2Br_2]I.H_2O$, as well as the **trans-salt;** P. Pfeiffer and M. Tapuach, **chromic dibromodiaquodipyridinoiodide,** $[CrPy_2(H_2O)_2Br_2]I.4H_2O$; P. Pfeiffer and T. G. Lando, complex salts of mercuric iodide with **chromic diiodobisethylenediaminoiodide,** $[Cr\ en_2I_2]I$; P. Pfeiffer and P. Koch, a complex salt of mercuric iodide with **chromic cisthiocyanatobisethylenediaminoiodide,** $[Cr\ en_2(SCy)_2]I.HgI$; P. Pfeiffer and A. Trieschmann, and H. Schwarz, **chromic oxalatobisethylenediaminoiodide,** $[Cr\ en_2(C_2O_4)]I$; S. M. Jörgensen, **chromic hydroxydecamminopentaiodide,** $[Cr(OH)(NH_3)_{10}]I_5.H_2O$; F. Pintus prepared **chromic trisethylenediaminotriiodide,** $[Cr\ en_3]I_3$. S. M. Jörgensen, **chromic hydroxydecamminohydroxydichlorodiiodide,** $[Cr_2(OH)(NH_3)_{10}]Cl_2I_2(OH)$, and **chromic hydroxydecamminochlorotetraiodide,** $[Cr_2(OH)_6(NH_3)_{10}]ClI_4.H_2O$; P. Pfeiffer and R. Stern, **chromic dihydroxyquaterethylenediaminotetraiodide,** $[Cr_2(OH)_2\ en_4]I_4.2\frac{1}{2}H_2O$; S. M. Jörgensen, **chromic trihydroxyaquohexamminotriiodide,** $[Cr_2(OH)_3(H_2O)(NH_3)_6]I_3.H_2O$; R. F. Weinland and E. Büttner, **chromic hexacetatodihydroxytriamminoiodide** $[Cr_3(CH_3COO)_6(NH_3)_3(HO)_2]I$; R. F. Weinland and E. Gussmann, **chromic hexacetatodihydroxytripyridinoiodide,** $[Cr_3(CH_3COO)_6Py_3(OH)_2]I$; and P. Pfeiffer and W. Vorster, **chromic hexahydroxysexiesethylenediaminohexaiodide,** $[Cr_4(OH)_6en_6]I_6.H_2O$, and an addition product with mercuric iodide.

S. M. Jörgensen prepared the complex **chromic chloropentamminodiiodomercuriiodide,** $[Cr(NH_3)_5Cl]I_2.HgI$, as well as $[Cr(NH_3)_5Cl]I_2.2HgI_2$; P. Pfeiffer, **chromic diiodobisethylenediaminoiodomercuriiodide,** $[Cr\ en_2I_2]I.HgI_2$; P. Pfeiffer and P. Koch, **chromic dithiocyanatobisethylenediaminoiodomercuriiodide,** $[Cr\ en_2(SCy)_2]I.HgI_2$; and P. Pfeiffer and W. Vorster, **chromic hexahydroxysexiesethylenediaminohexaiodomercuriiodide,** $[Cr_4(OH)_6en_6]I_6.2HgI_2.8H_2O$.

As indicated above, J. Inglis,[3] and P. Guyot obtained no evidence of the formation of an oxyiodide by the action of hydriodic acid on potassium chromate. H. Giraud said that an oxyiodide is formed as a deep red, oily liquid, boiling at 149°, by the action of sulphuric acid on a mixture of potassium dichromate and iodide. H. Rose found that iodine, not **chromyl iodide,** is formed; nor could S. G. Rawson verify this, nor could he obtain an oxyiodide by the action of calcium iodide on chromyl chloride in a sealed tube; by the action of the vapour of chromyl chloride on ethyl iodide, or by the action of hydrochloric acid, acetic acid, or hydrofluosilicic acid on a mixture of potassium iodide, chromium trioxide, and solid zinc chloride. I. Walz obtained some iodate by the action of chromic acid on iodine. H. S. Fry treated chromium trioxide with acetyl iodide and obtained only iodine. There was no evidence of the formation of chromyl iodide.

According to P. Guyot, when potassium chromate is treated with colourless

hydriodic acid, garnet-red crystals of **potassium iodochromate,** $KCrO_3I$, are produced. If the salt contains an excess of iodine it may have a brown tint, but on exposure to the air it gradually assumes its normal colour. It is decomposed in the presence of water into hydriodic acid and potassium dichromate. When heated it gives off iodine copiously; on boiling it with hydriodic acid more iodine is given off, potassium iodide and chromic iodide remaining behind.


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## § 28. Chromium Sulphides

O. Schumann [1] made some observations on the relative affinities of chromium and the metals for sulphur and oxygen. According to A. Moberg, when chromous chloride is treated with ammonium sulphide, a black precipitate—presumably **chromous sulphide** or **chromium monosulphide,** CrS—is formed; E. M. Péligot obtained it by the use of potassium sulphide and observed that the precipitate is insoluble in an excess of the precipitant. M. Traube observed that the sulphide occurs among the products of the reduction of chromic sulphate heated in hydrogen. H. Moissan observed that when chromous chloride is heated to 440° in hydrogen sulphide, this sulphide is formed; this is also the case when chromic sulphide is heated in hydrogen. A. Moulot obtained this sulphide by heating chromium in an atm. of hydrogen sulphide in an electric furnace. The black mass prepared at a high temp. forms opaque, prismatic crystals of sp. gr. 4·08. The black, non-crystalline powder has a sp. gr. 3·97. W. F. de Jong and H. W. V. Willems found that the

crystals of the monosulphide, prepared by heating sulphur and chromium at 600°, have an X-radiogram in agreement with a hexagonal lattice with $a$=3·44 A., and $c$=5·67 A.; and sp. gr. 4·85. M. Picon gave 1550° for the m.p. The crystals scratch quartz. M. Picon found that chromous sulphide is more resistant to the action of carbon at a high temp., in vacuo, than is the corresponding oxide. The sulphide melts without dissociation at 1550°. E. Wedekind and C. Horst gave $28{\cdot}4\times10^{-5}$ mass units for the magnetic susceptibility at 19·5°. Chromous sulphide is easily attacked by oxidizing agents, but not by reducing agents. Chromous sulphide is but slightly reduced when heated to 1200° in hydrogen; with oxygen, at a red-heat, chromic oxide and sulphate, and sulphur dioxide are formed; when heated in air, it glows, forming chromic oxide, but no sulphur is obtained; with water-vapour, chromic oxide and hydrogen sulphide are formed; with fluorine, combination occurs with incandescence, and similarly also with hydrogen fluoride; at 340°, chlorine forms chromic chloride; and carbon, in an electric furnace, forms a product free from sulphur. Molten potassium hydroxide or carbonate produces sulphate and chromate. According to M. Houdard, by heating a mixture of aluminium (7 grms.) and chromium (5·6 grms.) in a current of hydrogen sulphide, a black, crystalline mass is obtained, which evolves hydrogen sulphide with water, giving a deposit of alumina and leaving a reddish-black, crystalline residue, which, when washed with dil. hydrochloric acid, corresponds with **chromous sulphoaluminate,** $Al_2S_3.CrS$, or $Cr(AlS_2)_2$. Its optical properties resemble those of the spinels, and the crystals have the cubic structure. If excess of chromium is used, the sesquisulphide seems to be formed and the crystalline mass obtained is only with difficulty attacked by dil. hydrochloric acid, whilst nitric acid slowly destroys the double compound, leaving a black, crystalline residue of CrS. For chromous sulphochromite, *vide infra.*

H. Moissan observed that **chromic sulphide,** or **chromium hemitrisulphide,** or **chromium sesquisulphide,** $Cr_2S_3$, can be formed by the direct union of the elements, for chromium filings at 700° unite with sulphur vapour to form this compound; and it is also formed when hydrogen sulphide is passed over chromium at 1200°. J. J. Berzelius prepared this compound by heating an intimate mixture of sulphur and chromic oxide in vacuo; and L. R. von Fellenberg melted a mixture of chromic oxide, sulphur, and potassium carbonate. O. Harten obtained it by passing hydrogen sulphide over white-hot chromic oxide, or chromium trioxide. O. Schumann working at a lower temp. obtained only a 25 per cent. conversion. H. Moissan added that the reaction with chromic oxide, not previously calcined, sets in at about 440°. W. Müller obtained a large proportion of chromic oxide by passing hydrogen sulphide over heated potassium chromate, and extracting the potassium sulphide with water. J. L. Lassaigne heated a mixture of chromic chloride and sulphur at a red-heat, but, added J. J. Berzelius, the reaction is incomplete. J. von Liebig obtained chromic sulphide by passing hydrogen sulphide over strongly heated chromic chloride. J. J. Berzelius prepared the sulphide by melting chromic oxide and potassium pentasulphide at a high temp., and extracting the alkali sulphide with water. R. Schneider recommended preparing chromic sulphide by treating sodium sulphochromite with dil. hydrochloric acid, and heating the well-washed product in a current of carbon dioxide. F. Wöhler, and C. Brunner heated potassium chromate with potassium polysulphide, when, according to A. Schafarik, a complex alkali chromic sulphide is probably formed. K. Brückner found that when a mixture of chromic oxide and sulphur is heated in air, the oxide is not decomposed; chromium trioxide inflames and forms chromic oxide with a small proportion of sulphide; potassium chrome-alum with a prolonged heating forms chromic oxide and potassium sulphate, but if the mixture is heated for only a short period, a potassium and chromium sulphide is formed—*vide supra,* for the action of sulphur on chromates. H. Rose obtained chromic sulphide by passing the vapour of carbon disulphide over heated chromic oxide; W. Müller passed the vapour over heated potassium chromate and extracted the alkali sulphide by water; a large

proportion of chromic oxide is formed if ammonium chromate is employed. E. Kopp obtained a pyrophoric mixture by reducing chromic sulphate in hydrogen; M. Traube showed that the black product is a mixture of chromic sulphide and oxide. M. Traube obtained some sulphide by heating acid chromic sulphate in dry hydrogen sulphide; A. Moulot heated the sulphate mixed with potassium polysulphide; and K. Brückner, with sulphur. H. Moissan heated chromic oxalate in hydrogen sulphide; and R. Schneider heated the higher chromium sulphides—*e.g.* $Cr_4S_7=2Cr_2S_3+S$.

Analyses of chromic sulphide in agreement with the formula $Cr_3S_3$ were reported by L. R. von Fellenberg, O. Harten, A. Gautier and L. Hallopeau, and A. Mourlot. A. Schafarik, W. Müller, and M. Traube obtained rather too high a proportion of sulphur. J. L. Lassaigne's analysis must have been made on a very impure sample. According to the temp. at which it has been prepared, chromic sulphide appears as a black or dark grey powder; or in bright black, or greyish-black crystals in some cases resembling graphite. A. Schafarik gave 2·79 to 3·77 for the sp. gr. of the crystals. If heated in the absence of air, H. Moissan observed that chromous sulphide is formed. M. Picon found that chromic sulphide loses sulphur at 1350°, melts at 1550°, and then has a composition $CrS_{1·06}$. A. Karl said that the sulphide is triboluminescent. When the powder is used as anode in the electrolysis of 2 per cent. sulphuric acid, K. Fischbeck and E. Einecke found that as hydrogen sulphide is formed, tervalent chromium passes into soln. O. Stelling studied the X-ray spectrum. E. Wedekind and C. Horst gave $23·28\times10^{-6}$ mass units for the magnetic susceptibility. M. Traube, A. Schafarik, and J. L. Lassaigne observed that chromic sulphide burns like a pyrophorus when heated in air or oxygen forming chromic oxide—W. Müller said that some green basic sulphate is formed. H. V. Regnault observed that with water vapour, hydrogen sulphide and a little chromic oxide are formed. H. Rose said that chromic sulphide is scarcely attacked by chlorine even at a high temp.; but J. J. Berzelius, H. Moissan, L. R. von Fellenberg, and O. Harten observed that the sulphide is partially decomposed by chlorine at ordinary temp., but decomposition into chromic chloride is complete at higher temp. W. Müller observed only a slight action with hydrochloric acid. J. Milbauer and E. Tucek studied the action of sulphur dioxide on the heated sulphide. According to J. J. Berzelius, some forms of chromic sulphide are decomposed by nitric acid, while other forms are attacked with difficulty. A. Schafarik observed that fuming nitric acid does not attack the sulphide in the cold, but the boiling acid readily decomposes the sulphide, and J. L. Lassaigne said that the boiling acid has very little action. H. Moissan found that nitric acid, or aqua regia attacks the sulphide with difficulty, while J. L. Lassaigne said that aqua regia converts it into chromic chloride and sulphuric acid. F. Göbel found that chromic sulphide is decomposed when heated in carbon monoxide, and carbon disulphide is formed. J. L. Lassaigne found that with fused potassium nitrate it forms potassium chromate and sulphate; but J. J. Berzelius said that it is not dissolved by soln. of potassium hydroxide or sulphide. S. M. Jörgensen treated a soln. of chromic chloropentamminodichloride with ammonium polysulphide; on adding alcohol, and allowing the turbid liquid to stand in a dark place, he obtained brick-red, rhombic plates of **chromic chloropentamminopentasulphide,** $[Cr(NH_3)_5Cl]S_5$. It is sparingly soluble in cold water, and freely soluble in hot water. It is decomposed by hydrochloric acid. S. M. Jörgensen treated chromic trihydroxyaquohexamminotrichloride with ammonium polysulphide, and obtained cinnabar-red, octahedral crystals of **chromic trihydroxyaquohexamminohemienneasulphide,** $[Cr_2(OH)_3(H_2O)(NH_3)_6]_2S_{11}.2H_2O$.

The formation of complex sulphides was studied by M. Gröger, H. Moissan, and R. Schneider. These salts can be regarded as **sulphochromites,** $M'CrS_2$, or salts of **hydrosulphochromous acid,** $HCrS_2$, or $H_2Cr_2S_4$. This acid was reported by R. Schneider to be formed as an unstable product when sodium sulphochromite is treated with dil. hydrochloric acid in the absence of air. It forms $Cr_2S_4$ when exposed to air; and, when heated in the absence of air, it furnishes chromic oxide

and hydrogen sulphide. If potassium sulphotetrachromite, $K_2Cr_4S_7$, be similarly treated with dil. hydrochloric acid, grey crystals of **hydrosulphotetrachromous acid,** $H_2Cr_4S_7$, are formed. The crystals retain the form of the original crystals. The acid decomposes into hydrogen and chromic sulphides when heated in a current of carbon dioxide; it is unstable in air, forming water and the sulphide $Cr_4S_7$.

M. Gröger prepared **sodium sulphochromite,** $NaCrS_2$, by heating to redness a mixture of chromium hydroxide, sodium carbonate and sulphur (1 : 9 : 11) in a porcelain crucible until the excess of sulphur is expelled. The cold mass is extracted with water, and the residue washed with dil. soda-lye, then with alcohol, and finally with absolute alcohol. R. Schneider heated a mixture of potassium and sodium carbonates, potassium chromate, and sulphur; and F. J. Faktor, a mixture of sodium chromate and thiosulphate. E. Kunheim obtained it by heating a mixture of sodium and chromic sulphates and carbon in the electric arc. The dark red powder was found by R. Schneider to consist of dark brick-red, hexagonal plates of sp. gr. 2·55 at 15°. If heated in the absence of air it suffers no change. It is stable in air at ordinary temp., but when heated in air, it gives off sulphur dioxide forming chromic oxide and sodium sulphate. It is insoluble in water, but is decomposed by aerated water. R. Schneider obtained hydrosulphochromous acid by the action of dil. hydrochloric acid in the absence of air, and when exposed to air, $Cr_2S_4$ is formed. M. Gröger found that sodium sulphochromite is not attacked by conc. hydrochloric acid; cold conc. sulphuric acid is without action, but the hot acid decomposes the salt; nitric acid, and aqua regia decompose the salt forming chromic and sodium sulphates. The salt is not attacked by soln. of sodium hydroxide or sulphide.

J. J. Berzelius treated a soln. of potassium chromate with hydrogen sulphide, and obtained a dark brown liquid and chromic oxide. The liquid was thought to contain a sulphide of chromium and potassium; it deposits chromic sulphide when exposed to air, or when treated with acids; but the precipitate is decomposed by the liquid, forming, in air, potassium chromate, and sulphur. J. Milbauer obtained greyish-green crystals of **potassium sulphochromite,** $KCrS_2$, or $K_2Cr_2S_4$, by treating chromic oxide with molten potassium thiocyanate. It is stable in air, but when roasted it forms sulphur dioxide and chromic oxide; it is insoluble in water and hot hydrochloric acid, but freely soluble in aqua regia. According to R. Schneider, **potassium sulphotetrachromite,** $K_2Cr_4S_7$, is obtained by fusing potassium chromate (1 part) with potassium carbonate (24 parts) and sulphur (24 parts) for 20 minutes at a bright red-heat, allowing the mass to cool slowly, and washing it thoroughly but rapidly with cold water. It forms reddish to bluish-grey hexagonal plates with metallic lustre, and has a sp. gr.=2·77 at 15°. When four times as much chromate is used in proportion to the carbonate and sulphur, or a weight of chromium hydroxide equal to this, a grey powder is left instead of crystals; prolonged washing of this powder with hot water leaves pure chromic sulphide, $Cr_2S_3$, as J. J. Berzelius stated long ago. Potassium sulphotetrachromite is stable in air; it loses potassium sulphide slowly when it is washed with water; at a red-heat in a current of hydrogen, it loses one-seventh of its sulphur, leaving steel-blue crystals of **potassium sulphodichromite,** $KCr_2S_3$, or $K_2Cr_4S_6$, which retain the form of the sulphotetrachromite. When this compound is heated in air, it loses sulphur dioxide and leaves behind chromic oxide and potassium sulphide. Aq. soln. of potassium hydroxide or ammonia have little action; nitric acid, and aqua regia decompose it with the liberation of sulphur; hydrochloric acid, in the absence of air, forms the acid $H_2Cr_4S_7$.

M. Gröger precipitated **copper sulphochromite,** $Cu(CrS_2)_2$, from a soln. of the sodium salt by the addition of copper sulphate; R. Schneider used modifications of the process. Copper sulphochromite is not attacked by water, or hydrochloric acid; but is easily decomposed by warming with nitric acid or aqua regia. M. Gröger prepared **silver sulphochromite,** $AgCrS_2$, or $Ag_2Cr_2S_4$, as a black powder, by adding silver nitrate to a soln. of the sodium salt. R. Schneider used a modifica-

tion of the process. M. Gröger could not prepare calcium, strontium, or barium sulphochromite, by an analogous process. He obtained zinc sulphochromite, $Zn(CrS_2)_2$, by heating a mixture of zinc chromate and sulphur in hydrogen; and also by treating a soln. of chromic sulphate and zinc sulphate with ammonia, and heating the dried product in hydrogen, and then admixed with sulphur. The violet-brown mass is insoluble in water and hydrochloric acid, but is decomposed by nitric acid. The corresponding **cadmium sulphochromite,** $Cd(CrS_2)_2$, was similarly prepared. M. Gröger prepared **stannous sulphochromite,** $Sn(CrS_2)_2$, by the action of stannous chloride on a soln. of the sodium salt. It is not attacked by water or hydrochloric acid, but is oxidized by nitric acid. M. Gröger, and R. Schneider obtained **lead sulphochromite,** $Pb(CrS_2)_2$, by adding lead nitrate to a soln. of sodium sulphochromite. M. Gröger heated hydrated chromic oxide with sulphur in a current of hydrogen and obtained a greyish-black powder of **chromous sulphochromite,** $Cr(CrS_2)_2$, or $Cr_3S_4$. It is insoluble in water, boiling hydrochloric acid, and dil. sulphuric acid, but it is soluble in nitric acid with the separation of sulphur, and the formation of chromic sulphate and nitrate. It glows when heated in air, forming sulphur dioxide and chromic oxide. E. Wedekind and C. Horst said that its sp. gr. is 3·54 at 14°; E. Wedekind and T. Veit said that it is feebly magnetic; and E. Wedekind and C. Horst gave for the magnetic susceptibility $33{\cdot}26\times10^{-6}$ mass units. M. Gröger obtained chocolate-brown **manganese sulphochromite,** $Mn(CrS_2)_2$, by heating a mixture of sulphur and manganese and chromic oxides in an atm. of hydrogen. Similarly with black **ferrous sulphochromite,** $Fe(CrS_2)_2$, which was also obtained by treating a soln. of sodium sulphochromite with a soln. of a ferrous salt. The meteoritic mineral called **daubréelite,** found by J. L. Smith in meteoritic irons, is a ferrous sulphochromite, $FeS.Cr_2S_3$, or $Fe(CrS_2)_2$. Observations were also made by F. Zambonini, and A. Brezina and E. Cohen. S. Meunier synthesized it by the action of hydrogen sulphide on a red-hot mixture of ferrous and chromic chlorides, or on a mixture of iron and chromium. By treating a soln. of sodium sulphochromite with a cobalt salt, M. Gröger prepared **cobalt sulphochromite,** $Co(CrS_2)_2$, and similarly, by using a nickel salt soln., **nickel sulphochromite,** $Ni(CrS_2)_2$.

Other chromium sulphides have been reported. M. Gröger's **chromium tritatetrasulphide,** $Cr_3S_4$, as indicated above, is considered to be **chromium sulphochromite.** E. Wedekind and C. Horst gave $33{\cdot}26\times10^{-6}$ for the magnetic susceptibility of $Cr_3S_4$ at 15·5°. As indicated above. R. Schneider obtained **chromium tetritaheptasulphide,** $Cr_4S_7$, as a decomposition product of $H_2Cr_4S_7$; and chromium disulphide, $CrS_2$, or $Cr_2S_4$, as a decomposition product of $H_2Cr_2S_4$. T. L. Phipson reported **chromium hemiheptasulphide,** $Cr_2S_7$, to be formed by passing hydrogen sulphide into a soln. of potassium dichromate sat. with ammonia, and adding hydrochloric acid to the filtrate. G. Bender was unable to confirm this result, and said that the alleged sulphide is a mixture of sulphochromite and hydrated chromic oxide.

O. Nordenskjöld reported a complex salt, **mercuric chromium trithiocyanatohexasulphodiammine,** $Cr(SCy)_3.2NH_3.6HgS$, to be formed by the action of mercuric sulphide on mercuric tetrathiocyanatodiamminochromiate.

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## § 29. Chromium Sulphates

E. M. Pèligot [1] found that when the brown product obtained by reducing chromic chloride with potassium is treated with dil. sulphuric acid, some hydrogen is evolved, and a soln. of **chromous sulphate,** $CrSO_4$, is formed. H. Moissan treated chromium amalgam with dil. sulphuric acid; and A. Burger dissolved chromium from the aluminothermite process in sulphuric acid of sp. gr. 1·16 with the exclusion of air, at 90° to 100°, and obtained a blue soln. of chromous sulphate contaminated with some chromic sulphate. According to A. Asmanoff, an aq. soln. of chromic sulphate is reduced electrolytically at a lead cathode in an atm. of hydrogen. When reduction is complete, the chromous sulphate is precipitated by alcohol, washed with alcohol and ether, and dried in a current of hydrogen. The product is stable in dry air. H. Moissan obtained a white, crystalline powder of the *monohydrate* by treating moist chromous acetate with conc. sulphuric acid in the absence of air. This hydrate is more stable in air than is the heptahydrate; it is converted by a little water into the heptahydrate; and at a red-heat it forms chromic oxide, and sulphur dioxide and trioxide. B. Cabrera and S. P. de Rubies studied the magnetic qualities of the salt; and F. Allison and E. J. Murphy, the magneto-optic properties.

J. M. van Bemmelen observed that a sample kept for a year in a sealed tube exploded. H. Moissan obtained the *heptahydrate* by dissolving chromous acetate in dil. sulphuric acid in an atm. of carbon dioxide, and cooling the blue soln. The blue crystals are isomorphous with heptahydrated ferrous sulphate. They are soluble in water; and slightly soluble in alcohol. Conc. sulphuric acid converts the salt into the monohydrate. The aq. soln. is not wholly converted into chromic sulphate by boiling. The crystals and the blue soln. readily absorb oxygen from air, and with nitric oxide are coloured brown. According to A. Asmanoff, in presence of platinum as catalyst, the soln. oxidizes with evolution of hydrogen, the reaction being unimolecular. Sulphuric acid accelerates the reaction, but to a less extent than does hydrochloric acid. In absence of platinum, there is no measurable evolution of hydrogen with sulphuric acid present even in conc. up to 10*N*, although the reaction takes place to some extent in presence of hydrochloric acid. In the latter case, the oxidation is accelerated by ammonium chloride. Very rapid oxidation takes place in ammonia soln., especially in presence of ammonium salts, which prevent the precipitation of chromous hydroxide. The reaction is then no longer unimolecular, but is autocatalyzed by the chromic ion. M. Berthelot found that the blue soln. mixed with ammonia and ammonium chloride readily absorbs acetylene and is thereby decolorized; after a short time the soln. becomes rose-red, and deposits a precipitate giving off ethylene. The acidic soln. absorbs no more acetylene than is the case with water.

According to C. Laurent, blue crystals of **ammonium chromous sulphate,** $(NH_4)_2SO_4.CrSO_4.6H_2O$, are formed by evaporating a soln. of the component salts

in an atm. of carbon dioxide. The blue crystals resemble the double sulphates of the magnesium series. The salt is freely soluble in water; 100 c.c. of a sat. aq. soln. contain 55 grms. of the salt at 20°. The salt is insoluble in alcohol. It readily oxidizes in air. W. Traube and W. Passarge obtained **hydrazine chromous sulphate,** $(N_2H_4)_2H_2SO_4.CrSO_4$, by the action of hydrazine sulphate on a soln. of sulphuric acid and of chromous acetate in air-free water, covered with a layer of light petroleum as a protection from air. The precipitate is washed successively with water, alcohol and ether. C. Laurent prepared **sodium chromous sulphate,** $Na_2SO_4.CrSO_4.4H_2O$, by the action of sodium acetate on a sulphuric acid soln. of sodium sulphate. E. M. Péligot obtained rhombic prisms of **potassium chromous sulphate,** $K_2SO_4.CrSO_4.6H_2O$, by adding alcohol to a mixture of chromous chloride and a cold, sat. soln. of potassium sulphate. The crystals are isomorphous with those of potassium ferrous sulphate. C. Laurent also prepared **rubidium chromous sulphate,** $Rb_2SO_4.CrSO_4.6H_2O$; **cæsium chromous sulphate,** $Cs_2SO_4.CrSO_4.6H_2O$; **magnesium chromous sulphate,** $MgSO_4.CrSO_4.14H_2O$; **zinc chromous sulphate,** $ZnSO_4.CrSO_4.14H_2O$; as well as complexes of manganese and ferrous sulphates (*q.v.*).

The anhydrous **chromic sulphate,** $Cr_2(SO_4)_3$, reported by A. Schrötter [2] to be formed by heating a basic sulphate with conc. sulphuric acid until the acid begins to fume was supposed, by M. Traube, L. and P. Wöhler and W. Plüddemann, and M. Siewert, to be the acid salt. T. Klobb, however, obtained the red sulphate of the composition, $Cr_2(SO_4)_3$, by heating ammonium chromic sulphate with boiling, conc. sulphuric acid. A. Schrötter, and M. Siewert obtained it by heating the hydrated salt over 280° in a current of carbon dioxide. M. Siewert's, and T. Klobb's analyses agreed with the formula $Cr_2(SO_4)_3$; and A. Recoura gave the formula $Cr_2(SO_4)_6Cr_2$ in agreement with that for $Cr_2(SO_4)_6Fe_2$. The powder is rose-coloured in daylight, and green by gas-light. P. A. Favre and C. A. Valson gave 2·743 for the sp. gr. at 17·2°; A. Sénéchal, 2·221 at 30°; E. Moles and M. Crespi, 3·712 at 25°/4°; while L. F. Nilson and O. Pettersson gave 3·012 for the sp. gr.; 130·27 for the mol. vol.; 0·1718 for the sp. ht.; and 67·41 for the mol. ht. K. Friedrich found that the thermal decomposition curve is somewhat complex; the gases, sulphur dioxide and trioxide and oxygen, have one atm. press. at 750°. R. Robl observed but a faint luminescence in ultra-violet light. E. Kunheim studied the decomposition of mixtures of chromic sulphate and carbon in the electric arc.

According to A. Schrötter, crystals of the **violet hydrate,** which is provisionally taken to be the *octodecahydrate*, $Cr_2(SO_4)_3.18H_2O$, are obtained by allowing to stand for a few weeks a soln. of hydrated chromic oxide in the calculated quantity of conc. sulphuric acid. The soln. in water is dark blue by reflected light, and ruby-red by transmitted light; alcohol precipitates from the soln. a pale violet, crystalline powder and the soln. becomes colourless—only when there is an excess or a deficiency of acid does the soln. remain green. To obtain good crystals, he recommended dissolving the crystalline powder in a moderate quantity of water, adding dil. alcohol to the stage at which precipitation begins, and leaving the soln. to evaporate spontaneously in a vessel covered by a bladder. H. Löwel dissolved 50 grms. of dried hydrated chromic oxide in 125 grms. of conc. nitric acid; added 125 c.c. of water, and boiled for 15 min. When the liquid was cold, he added a cold soln. of 75 grms. of conc. sulphuric acid in 150 grms. of water, followed by 1200 grms. of alcohol. The precipitated crystalline powder was washed with alcohol, and dried between bibulous paper. H. Baubigny used a similar process. M. Traube allowed alcohol to drop into a soln. of chromium trioxide, conc. sulphuric acid, and water (1 : 1·5 : 3); at the end of the reduction, the chromic sulphate is precipitated by alcohol. If the temp. rises during the reduction, the green sulphate is formed. This can be converted to the violet form by boiling the liquid with nitric acid. T. W. Richards and F. Bonnet, and M. A. Graham used this process. M. Traube also obtained the violet sulphate by passing a mixture of chromic acid, conc. sulphuric acid, and water (1 : 1·5 : 2·25) into a wide basin in which a porcelain crucible containing

ether is placed. Crystals of the sulphate are formed in a few hours. To complete the reduction, a few drops of alcohol may be added. G. O. Higley prepared this salt by adding 100 grms. of chrome-alum to a cold soln. of 100 c.c. of conc. sulphuric acid, and 330 c.c. of water; and pouring 260 c.c. of conc. sulphuric acid, with constant stirring, into the filtered soln. at 15° to 20°. Hydrochloric acid can be used as solvent for the alum. R. F. Weinland and R. Krebs obtained good crystals from a soln. of a mol of alum in 60 to 80 mols of $H_2SO_4$ in 95 per cent. soln. by cooling and evaporation in a vacuum desiccator; they also obtained the salt by adding alcohol to a soln. of chromium chlorosulphate; F. Krauss and co-workers used a similar process. A. Werner and A. Gubser obtained the salt by adding sulphuric acid to a violet soln. of chromic chloride; and P. M. Strong, by treating the mother-liquor from the preparation of the polychromosulphuric acid with the necessary quantity of green sulphate and sulphuric acid, concentrating the mixture on a water-bath; and allowing it to stand in the cold for 3 or 4 days to crystallize. E. Wydler also described the preparation of the salt.

There are differences of opinion about the water of crystallization. Analyses by G. O. Higley, A. Werner and A. Gubser, A. Étard, and M. Siewert correspond with the *hexadecahydrate*, $Cr_2(SO_4)_3.16H_2O$, for the air-dried salt; and by A. Sénéchal, with the *tetradecahydrate*, $14H_2O$. A. Schrötter said that the pentadecahydrate, $Cr_2(SO_4)_3.15H_2O$, is formed when the salt is dried at 35°. R. F. Weinland and R. Krebs obtained with all modes of preparation tried, needles and plates of the *heptadecahydrate*, $Cr_2(SO_4)_3.17H_2O$. A. Sénéchal obtained with the preparations with precipitated alcohol, $Cr_2(SO_4)_3.16{\cdot}0$ to $17{\cdot}5H_2O$, and after exposure to dry air, $Cr_2(SO_4)_3.14H_2O$; he also gave for the vap. press., $p$ mm. of differently hydrated salts, $Cr_2(SO_4)_3.nH_2O$:

| | | | | | | |
|---|---|---|---|---|---|---|
| $n$ | . . . | 17·25 | 16·55 | 15·77 | 15·05 | 14·78 |
| | 25·6° . | 20·1 | — | 11·0 | 11·1 | — |
| | 29·3° . | 24·4 | 17·4 | 14·0 | 13·8 | 12·8 |
| $p$ at | 34·0° . | 31·5 | 24·2 | 19·1 | 18·4 | 17·3 |
| | 38·5° . | 39·1 | 31·9 | 24·9 | 23·5 | — |
| | 40·4° . | 43·4 | — | 27·7 | 26·2 | — |

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From these results, A. Sénéchal concluded that hydrates with $17H_2O$, $16H_2O$, $15H_2O$, and $14H_2O$ are chemical individuals, and that the tetradecahydrate slowly loses water at room temp. and has, at 29·3°, a vap. press. of 3 mm. M. Siewert said that when the salt was dried for an hour in the sun, it contained $12H_2O$; G. D. van Cleeff, that when the octodecahydrate is dried over sulphuric acid, it loses 3·5 to $4{\cdot}0H_2O$, at 75° it changes colour, with the loss of more water, and at 100°, it retains $4H_2O$; A. Schrötter, that the salt dried at 100° has 5 to $6H_2O$; A. Recoura, that at 90°, it forms the green hydrate with $8H_2O$; A. Kling and co-workers said $5H_2O$; and A. Étard, A. Schrötter, and A. Colson added that at 100°, the salt melts in its water of crystallization and retains $6H_2O$ and solidifies into a green gummy mass. G. N. Wyrouboff found that when dried at 110°, the salt retains $5H_2O$, and it loses no more water even when heated to 150°. M. Siewert stated that at 280°, in a current of carbon dioxide, most of the water is driven off, and all is expelled below a red-heat. G. T. Gerlach made some observations on this subject; and for those of A. Sénéchal—*vide infra*. According to W. R. Whitney, and A. Sénéchal, all products with less than $12H_2O$ are not to be considered as hydrates of the violet sulphate. G. N. Wyrouboff represented the violet sulphate by the formula $Cr_2(OH_2)_4(OH_2)_2(SO_2)_3(OH_2)_6$; and W. R. Whitney represented it by the formula $[Cr_2(H_2O)_{12}](SO_4)_3 6H_2O$, or $[Cr(H_2O)_6]_2(SO_4)_3.6H_2O$, which is taken best to represent the properties of the salt in aq. soln. and in the solid state. E. Moles and M. Crespi found that $[Cr(H_2O)_6]_2(SO_4)_3.5H_2O$ lost 3 mols. of water at 18°; and $[Cr(H_2O)_6]_2(SO_4)_3.2H_2O$ lost 10·7 mols. of water at 140°. According to F. Krauss and co-workers, the octodecahydrate furnishes the *enneahydrate*, $Cr_2(SO_4)_3.9H_2O$, which is stable between 30° and 100°, but the *trihydrate*, $Cr_2(SO_4).3H_2O$, has only a small range of existence. The three mols. of water are

combined as in the zeolites and are therefore given up slowly. Complete dehydration occurs at about 325°.

According to A. Schrötter, and R. F. Weinland and R. Krebs, the violet hydrate forms octahedral crystals belonging to the cubic system. A. Schrötter gave 1·696 for the sp. gr. at 22°; and P. A. Favre and C. A. Valson, 1·867 at 15°. E. Moles and M. Crespi found the sp. gr. of $[Cr(H_2O)_6]_2(SO_4)_3.5H_2O$ to be 1·840 at 25°/4°, and the mol. vol. 375 to 379; and of $[Cr(H_2O)_6]_2(SO_4)_3.2H_2O$, 1·976 for the sp. gr. at 25°/4°, and 326 for the mol. vol. A. Schrötter observed that the violet salt is freely soluble in water; the percentage solubility is 54·65 per cent., but by analogy with violet hydrated chromic chloride, the solubility must depend on the equilibrium: violet sulphate⇌green sulphate. F. Krauss and co-workers observed that the dehydration curve showed breaks corresponding with 18-, 9-, 3·, and 0-hydrates. E. N. Gapon discussed some relationships of the m.p. P. A. Favre and C. A. Valson gave −3·255 Cals. for the heat of soln. per mol of $Cr_2(SO_4)_3.15H_2O$; and A. Recoura, −6·2 Cals. for a mol of $Cr_2(SO_4)_3.16H_2O$. The difference in the results may be due to differences in the proportions of the green and violet hydrates formed in different methods of preparation, etc. A. Sénéchal's results are in agreement with those of A. Recoura, for he found for the heat of soln. at 14° of the tetradecahydrate, −10·10 Cals.; for the pentadecahydrate, 8·3 Cals.; for the hexadecahydrate, −7·49 Cals.; and for the heptadecahydrate, 6·35 Cals. T. Dreisch studied the ultra-red absorption spectrum of soln. of chromic sulphate. E. Feytis said that there is no difference between the magnetic susceptibilities of the different hydrates, for the coeff. of magnetization are in all cases round about $1400\times10^{-6}$. G. Jäger and S. Meyer gave $31\times10^{-6}$ mass units for the magnetic susceptibility of the soln. at 18°; and O. Liebknecht and A. P. Wills, $15\times10^{-6}$ mass units at the same temp. V. N. Ipatieff and B. A. Mouromtseff found that soln. of chromic chloride are reduced by hydrogen under a press. of 200 atm. A. Mailfert studied the action of ozone. K. H. Butler and D. McIntosh found that the sulphate is insoluble in liquid chlorine and has no effect on the b.p. of the liquid. The violet crystals, said M. Traube, can be boiled with alcohol at 80° without passing into the green salt; on the other hand, A. Schrötter said that if a layer of alcohol be poured over the violet soln. contained in a narrow glass vessel, so as not to mix the liquids, the aq. soln. acquires a green colour starting from above and working downwards. This is attributed to the alcohol attracting or withdrawing water from the violet salt so as to form the green salt. According to A. Étard, cold monohydrated nitric acid, sulphuric acid, and phosphorus trichloride abstract water from the violet solid or soln. forming the green salt. The actual cause of the colour change is not certain. K. Schorlemmer investigated the oxidation of chromic salts to chromates by hydrogen dioxide. A. Violi found that molten sulphur converts the sulphate into chromic sulphide and sulphur dioxide. According to A. Recoura, complexes in which acetic anhydride replaces some of the water of hydrated salts are called *acetylated salts*; such an association, $Cr_2(SO_4)_3.4H_2O.4(C_2H_3O)_2O$, is formed by the slow action of finely powdered hydrated chromic sulphate on acetic anhydride.

According to A. Recoura, the **green hydrate,** which he regarded as the *hena-hydrate*, $Cr_2(SO_4)_3.11H_2O$, is obtained by reducing chromic acid in the presence of sulphuric acid, say, by pouring 40 c.c. of conc. sulphuric acid, and 35 c.c. of 95 per cent. alcohol into a mush of 50 grms. of chromium trioxide and 13 grms. of water. The product is dried in vacuo. A. Recoura obtained what he regarded as the *octohydrate*, $Cr_2(SO_4)_3.8H_2O$, by heating the violet sulphate to 100°. A. Étard, and A. Colson said that the product is a *hexahydrate*, and G. N. Wyrouboff, a *penta-hydrate*. According to A. Sénéchal, the air-dried violet hydrate, $Cr_2(SO_4)_3.14H_2O$, begins to turn green in vacuo at 30°, and in air at 55° with the simultaneous loss of water. If the product be dissolved in water, and the violet sulphate crystallized out by cooling the soln. with ice-water, there remains, on evaporating the soln. to dryness, hexahydrated $Cr_2(SO_4)_3.6H_2O$, or $[Cr_2(SO_4)_3(H_2O)_6]$. This loses water at

80°, forming the trihydrate, $Cr_2(SO_4)_3.3H_2O$, or $[Cr_2(SO_4)_3(H_2O)_3]$, and at the same time its solubility is reduced. The trihydrate loses water at 150°, forming a greyish-green and then a greyish-red product which is insoluble in water, and loses all its water at 400°. The mol. vols. of the sulphates with 3 to 14 mols. of water are additive; but not so with those containing less water. E. Moles and M. Crespi gave 2·429 for the sp. gr. of $Cr_2(SO_4.H_2O)_3$ at 25°/4°, and 145 for the mol. vol. They also found that it lost 3·01 mols. of water at 350°. F. Krauss and co-workers showed that the dehydration curve of the green hydrate is the *dodecahydrate*, $Cr_2(SO_4)_3.12H_2O$, and when heated, 2 mols. of water behave like zeolitic water; then the hexahydrate, $Cr_2(SO_4)_3.6H_2O$, is formed; and finally, at about 400°, the anhydrous green chromate is formed. All the water in the green, amorphous *pentadecahydrate*, $Cr_2(SO_4)_3.15H_2O$, is zeolitic, and is all lost at 400° and 100 mm. Barium chloride precipitates all the $SO_4$ from a cold soln. of the violet sulphate, but not completely from a warm soln.; the green soln. of the dodecahydrate gives up most of the $SO_4$ to barium chloride, and all is given up at 100°. The cold soln. of the green, amorphous pentadecahydrate gives no precipitate with barium chloride, but if the soln. be aged, or boiled for some time, sulphate is precipitated.

According to A. Recoura, the hygroscopic green sulphate is stable, but the green aq. soln. gradually becomes violet. A freshly prepared soln. is precipitated neither by a barium salt nor by sodium hydrophosphate so that it behaves neither like a sulphate nor like a chromium salt. Alkali hydroxides precipitate from the soln. a basic salt with only two sulphate-radicles, namely, $Cr_2O(SO_4)_2$; and the heat of formation is $Cr_2O_{3aq.}+2H_2SO_4=Cr_2O_3.2SO_{3aq.}$; and $Cr_2O(SO_4)_{2aq.}+H_2SO_4=-0{\cdot}2$ Cal. The heat of transformation from the dissolved violet to the green salt is −23·15 Cals., showing that the stable form is the violet salt. The isomerism between the green and violet sulphates is analogous to that between the green and violet chlorides or bromides. According to H. G. Denham, the green sulphate has twice the mol. wt. of the violet salt, and its formula is taken to be $[Cr_4(SO_4)_4](SO_4)_2$. It is strongly hydrolyzed in aq. soln. forming, in conc. soln., $[Cr_4(SO_4)_4](SO_4)(OH)_2$, and in dil. soln., $[Cr_4(SO_4)_4](OH)_4$. The transformation from the violet to the green sulphate is represented: $2Cr_2(SO_4)_3=[Cr_4(SO_4)_4](SO_4)_2$.

The basic or *modified sulphate* is a different case. Its soln. is obtained from the violet salt when heated, but it has not been obtained in the crystalline state—it furnishes a viscid syrup. The modified soln. is obtained by heating the violet soln. for a long time at 100°, and then cooling it rapidly. In the modified sulphate one-third of the sulphate can be precipitated by barium chloride. It is thought to be a complex base, $[Cr_4O(SO_4)_4](OH)_2$. A. Colson said that by heating a soln. of the violet salt, $Cr_2(SO_4)_3$, it is transformed into a pentasulphate, $HSO_4(CrSO_4)_2$–O–$(CrSO_4)_2.OH$, in which four of the $SO_4$-radicles are masked; if the boiling be continued a further hydrolysis occurs, and $SO_4Cr.O.O.Cr(SO_4)_2.O.CrSO_4$ is formed.

A. Colson said that there are three types of the green sulphate. These differ in their behaviour towards soln. of barium chloride, in their heats of formation, and in their sp. gr. The first type has *all three $SO_4$-radicles completely masked*, meaning that a soln. of a salt gives no precipitate with barium chloride. It is formed by the action of sulphur dioxide on a 5 per cent. soln. of chromic acid cooled by a freezing mixture; and also by evaporating a soln. of the green salt in sulphuric acid, extracting the unchanged violet salt by alcohol at 75°, and evaporating the liquid in vacuo. The green, hygroscopic, transparent plates, $Cr_2(SO_4)_3.6H_2O$, are soluble in alcohol at 75° but insoluble at 92°; the heat of formation is 33 cals.; and when the soln. has stood for about 3 days, it passes into a soln. of the second type in which two of the *three $SO_4$-radicles are masked*, meaning that barium chloride precipitates from the aq. soln. only one-third of the contained sulphate. B. Cabrera and S. P. de Rubies found that the electrical conductivity and unmasking of the $SO_4$-radicles of a soln. of the salt increase in a parallel way on keeping; no appreciable change in magnetic susceptibility occurs. The evaporation of the aged soln. in vacuo gives a salt, $Cr(SO_4)_3.8H_2O$, resembling that with three masked $SO_4$-

radicles. It loses water over phosphorus pentoxide in vacuo, and then consists of $Cr_2(SO_4)_3.7\frac{1}{2}H_2O$. Its heat of formation is 36·6 Cals. An isomeric form with two masked $SO_4$-radicles is said to be obtained by heating the violet sulphate to 90° and keeping the residue in water for 3 or 4 days below 5°. The two forms are said to differ in their heats of reaction with barium chloride, and in the electrical conductivity of their soln. In the third type *one only of the three $SO_4$-radicles is masked*, for, when the aq. soln. is treated with barium chloride, two-thirds of the contained sulphate is precipitated. This salt, $Cr_2(SO_4)_3.7\frac{1}{2}H_2O$, is prepared by the long-continued action of water on either of the two former types; or by precipitating hydrated chromic oxide from either soln., dissolving the product in sulphuric acid, and evaporating the soln. in vacuo. The heat of formation is 43·5 Cals.

It will be observed that the second and third types are formed by the progressive hydrolysis of the first type, and that there is simultaneously a change in the sp. gr., f.p., conductivity, and other properties of the soln. It is therefore assumed that the first type is to be regarded as $Cr_2(SO_4)_3.nH_2O$, or $[Cr_2(SO_4)_3].nH_2O$; the second, as $Cr_2(SO_4)_3(H_2O).nH_2O$, or $[Cr_2(H_2O)(SO_4)_2]SO_4.nH_2O$; and the third, as $Cr_2(SO_4)_3(H_2O)_2.nH_2O$, or $[Cr_2(H_2O)_2SO_4](SO_4)_2.nH_2O$; while the violet sulphate which has *no masked $SO_4$-radicles* is considered to be $Cr_2(SO_4)_3(H_2O)_3.nH_2O$, or $[Cr_2(H_2O)_3](SO_4)_3.nH_2O$. Each mol. of constitutional water is said to unmask one $SO_4$-radicle. According to the co-ordination theory, these four sulphates can be represented:

| $[Cr_2(H_2O)_{12}](SO_4)_3$ | $[Cr_2(H_2O)_{10}(SO_4)](SO_4)_2$ | $[Cr_2(H_2O)_8(SO_4)_2]SO_4$ | $[Cr_2(H_2O)_6(SO_4)_3]$ |
|---|---|---|---|
| | $\frac{1}{3}SO_4$-masked. | $\frac{2}{3}SO_4$-masked. | All $SO_4$-masked. |
| Violet sulphate. | Green sulphate. | | |

It is of course possible that intermediate products are formed. A. Colson supposed that a cold soln. of chromic sulphate is an equilibrium mixture of the violet sulphate and three green sulphates: $Cr_2(SO_4)_3.6H_2O$, $Cr_2(SO_4)_2(OH)(HSO_4)$, and $Cr_2(SO_4)(OH)_2(HSO_4)_2$. Whatever be the nature of the complex salts existing in soln., a state of equilibrium is ultimately attained and this is dependent on the concentration and temp. of the liquid. T. W. Richards and F. Bonnet showed that the reactions which occur are reversible, for if 0·25*N*-soln. of the green and violet salts are kept for a month at 30°, the amount of acid present, as indicated by the effect of the soln. on the inversion of cane-sugar, is the same in both cases, and approximates 0·043*N*. At 50°, the acid so produced approximates to about 0·10*N*, and at 100°, to 0·13*N*. This shows that the hydrolytic equilibrium varies with the temp. The kinetics of the reactions have not been closely investigated, but some observations by A. Colson showed that the reactions are very slow at ordinary temp.; they are faster with warmer soln., and at 100°, the transformation into the modified salt occupies a few minutes. A. Kling and co-workers measured the variation with time of the amount of sulphuric acid in the soln. precipitable by benzidine hydrochloride, the lowering of the f.p. and the electrical conductivity of 0·5*N*-green $Cr_2(SO_4)_4$. It was found that during the first twenty-four hours after the preparation of the soln. no sulphate precipitate is obtainable, but after that time the amount increases at first rapidly, and then gradually with passage of time. The mol. lowering of the f.p. and the electrical conductivity at first increase rapidly, even before the presence of the $SO_4''$-ion can be detected, and then attain a value which remains almost constant during the rest of the experiment. The green soln. of chromium sulphate tend towards a state of equilibrium, which is a function of the temp. and conc., and is the state towards which the violet soln. of the same conc. gradually pass. The properties of the chromium sulphate liquors with respect to their masked sulphate groups were studied by W. Schindler and K. Klanfer, E. Stiasny and co-workers, R. Reinicke, H. B. Merrill and co-workers, and G. Grasser.

By cooling conc. soln. of the violet salt crystals of that salt can be readily

obtained, but with soln. of the green salt, or of the so-called modified salt, only gummy or glassy masses are obtained. A. W. F. Sprung found the sp. gr. of a 24 per cent. soln. of the violet salt to be 1·1619, when that of the modified salt is 1·1486; and P. A. Favre and C. A. Valson gave 1·0600 for a $N$-soln. of the violet salt at 15°; and 1·0556 with the modified salt at 14·9°. G. T. Gerlach found the sp. gr. of green soln. to be greater than those of violet soln.; and he gave for the sp. gr. at 15°/15° of violet soln. with the following percentage proportions of $Cr_2(SO_4)_3$:

| $Cr_2(SO_4)_3$ . | 2·74 | 5·48 | 10·96 | 16·44 | 21·92 | 27·40 | 38·36 | 43·84 |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. { Green | 1·0275 | 1·0560 | 1·1150 | 1·1785 | 1·2480 | 1·3250 | — | — |
| Sp. gr. { Violet | — | 1·0510 | 1·1070 | 1·1680 | 1·2340 | 1·3055 | 1·4650 | 1·5530 |

According to A. Colson, an expansion occurs when a soln. of the violet salt passes into a soln. of the modified salt, and conversely the sp. gr. of a soln. of the green salt is intermediate between those of a soln. of the violet and of the modified salt. M. A. Graham found for the sp. gr. of soln. containing the following proportions of $Cr_2(SO_4)_3$ per litre:

| $Cr_2(SO_4)_3$ . | 0° | 10° | 20° | 30° | 40° | 50° |
|---|---|---|---|---|---|---|
| 40·14 . | 1·0394 | 1·0391 | 1·0369 | 1·0342 | 1·0292 | 1·0242 |
| 63·39 . | 1·0617 | 1·0602 | 1·0585 | 1·0585 | 1·0512 | 1·0462 |
| 83·77 . | — | — | 1·0763 | 1·0763 | 1·0680 | 1·0628 |
| 126·30 . | — | — | 1·1160 | 1·1160 | 1·1062 | 1·1002 |

The soln. develop a green colour at 40° and 50° so that the solute is doubtless a mixture of the green and violet salts. A. W. F. Sprung found that the viscosity of the violet soln. is much greater than is the case with eq. soln. of the modified salt; M. A. Graham obtained the following values for the viscosities of soln. containing the indicated number of grams of $Cr_2(SO_4)_3$ per litre:

| $Cr_2(SO_4)_3$ . | 10° | 20° | 25° | 30° | 40° | 50° |
|---|---|---|---|---|---|---|
| 19·64 . | 0·01577 | 0·01198 | 0·01062 | 0·00955 | 0·00776 | 0·00640 |
| 40·14 . | — | 0·01200 | 0·01065 | 0·00953 | 0·00774 | 0·00643 |
| 63·39 . | 0·01815 | 0·01355 | 0·01202 | 0·01076 | 0·00874 | 0·00787 |
| 83·77 . | 0·02028 | 0·01539 | 0·01396 | 0·01206 | 0·06975 | 0·00795 |
| 126·30 . | 0·02705 | 0·02072 | 0·01827 | 0·01621 | 0·01301 | 0·01041 |

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The same remarks apply to these results as to those given with respect to the sp. gr. at 40° and 50°. G. D. van Cleeff observed that in the dialysis of soln. of the salt the dialyzed part contains more acid than the part which remains; this was confirmed by M. D. Dougal, and T. W. Richards and F. Bonnet found that when a violet soln. of chromium sulphate is subjected to dialysis, the ratio $Cr/SO_4$ of the salt that has diffused and the salt that has remained in the dialyzer is the same in both. When, however, a green soln. of chromium is similarly treated, the ratio $Cr/SO_4$ diminishes in the diffused portion and increases in the dialyzer—an observation in favour of the view that the change from violet to green involves a hydrolysis with formation of free acid and a soluble basic salt.

The lowerings of the f.p. of violet soln. of the sulphate have been measured by A. Colson, H. G. Denham, and H. C. Jones and E. Mackay. The last-named found that for soln. with 0·025, 0·050, 0·10, and 0·250 mol per litre, the f.p. was —0·121°, —0·230°, —0·417°, and —1·029°. The results indicate that for the most dil. soln., five ions per mol. are formed. For 0·083$N$-soln. of the modified sulphate, H. G. Denham gave —0·420° for the f.p. of the modified soln., and A. Colson, for very rapidly cooled modified 0·1$N$- and 0·2$N$-soln., respectively —0·45° and —0·85°. H. G. Denham also measured the f.p. of sulphuric acid soln. The results show that the f.p. of the modified soln. is less than that of the violet soln., and if the hydrolysis of the salt is hindered by the presence of sulphuric acid, the apparent mol. wt. of the modified sulphate is greater than that of the violet salt. T. W. Richards and F. Bonnet, and M. A. Graham examined the f.p. of mixed soln. of chromium sulphate and cane-sugar. H. G. Denham observed that the f.p. of soln. of $\frac{1}{12}N$-soln. of violet and modified sulphate sat. with hydrated chromic oxide are respectively

$-0{\cdot}335°$ and $-0{\cdot}268°$. The results are taken to show the existence of a complex $Cr_4$-cation is formed, but migration experiments do not agree with the view that the complexity is due to the presence of such a complex. A. Colson found that soln. freshly prepared in the cold from the solid green sulphate show a small depression of the f.p. which rapidly rises until a value corresponding with that required for the violet soln. is attained. K. Flick studied the thermal decomposition of solid chromic sulphate.

According to A. Recoura, the heat of transformation of a mol of the dissolved green sulphate into the modified sulphate is 4·2 Cals., and into the violet sulphate, 23·15 Cals., so that the heat of transformation of a mol of the modified to the violet sulphate in soln., is 18·95 Cals. per mol. When a mol of dissolved sodium hydroxide is added to a mol of chromic sulphate in 12 litres of a modified soln., 15·61 Cals. are developed, while the addition of more sodium hydroxide develops only a little more heat; a mol of sodium hydroxide neutralizes only one-sixth of the sulphuric acid, and $\frac{1}{2}H_2SO_4$ in 12 litres of soln. with a mol of NaOH in 2 litres develops 15·63 Cals., it follows that about one-sixth the sulphuric acid was present in the soln. as free acid. A. Colson came to the same conclusion because he found that a mol of $Cr_2(SO_4)_3$ in modified soln. with $\frac{1}{2}Ba(OH)_2$ develops 18·7 Cals., while $\frac{1}{2}H_2SO_4 + \frac{1}{2}Ba(OH)_2$ develops 18·5 Cals. A mol of chromic sulphate in a green soln. with no precipitable $SO_4$, with 6 mols of potassium hydroxide develops 61·05 Cals., so that the heat of neutralization of the precipitated hydroxide with $3H_2SO_4$ is 33·12 Cals.; a similar soln. with one-third precipitable $SO_4$ develops with 6KOH, 57·6 Cals., and the heat of neutralization of the precipitated hydroxide with sulphuric acid is 36·6 Cals. Likewise with a mol of chromic sulphate with two-thirds precipitable $SO_4$ and 6KOH develops 43·5 Cals. With the violet soln. where all the $SO_4$ is precipitable, each $SO_4$ develops 6·65 Cals., for $H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl + 9{\cdot}5$ Cals. Otherwise expressed, with a mol of $Cr_2(SO_4)_3$ in modified soln., the addition of $\frac{1}{2}$ a mol of $BaCl_2$ develops 7·20 Cals. per mol of $BaCl_2$, and with another $\frac{1}{2}$ mol of $BaCl_2$, 7·06 Cals. per mol of $BaCl_2$; and with yet another $\frac{1}{2}$ mol of $BaCl_2$, 0·15 Cal. Accordingly, only one-third of the total sulphate reacts with barium chloride. Using a mol of $Cr_2(SO_4)_3$ in an aged green soln., the addition of one mol of $BaCl_2$ develops 7·1 Cals.; 2 mols, 14·1 Cals.; and 3 mols, 14·7 Cals. This shows that two-thirds of the total $SO_4$ is precipitated. According to A. Kling and co-workers, a fresh soln. of a mol of chromic sulphate, in ice-cold water, exhibits no thermal change.

L. R. Ingersoll found for Verdet's constant for the electro-magnetic rotatory power for light of wave-length 0·8, 1·0, and 1·25$\mu$, respectively 0·0067, 0·0045, and 0·0028 for soln. of chromic sulphate of sp. gr. 1·140. The absorption spectra of violet and green soln. of chromic sulphate were examined by D. Brewster, H. F. Talbot, W. N. Hartley, J. M. Hiebendaal, O. Knoblauch, W. Böhlendorff, A. Étard, G. Massol and A. Faucon, Y. Shibata and H. M. Vernon. H. C. Jones, and W. W. Strong found that with soln. of the violet sulphate at 5°, the three characteristic chromium bands appear—*viz.*, the ultra-violet band extending to $\lambda=2800$; the bluish-violet band from $\lambda=4100$ to 4450; and the yellowish-green band from $\lambda=5500$ to $\lambda=6200$. The bands at $\lambda=6800$ are very faint. The absorption in the visible spectrum is very strong. At 82°, the ultra-violet band extends to $\lambda=2900$, the bluish-violet band from $\lambda=4100$ to 4550, and the yellowish-green band from $\lambda=5500$ to 6300. The effect of a rise of temp. is therefore very small, usually involving a shifting of the long wave-length edges of all three bands towards the red. M. A. Graham found that the ultra-violet absorption spectra of green and violet soln. indicate that the change in colour which occurs is not due to simple hydrolysis, but is the result of a process involving both hydrolysis and a change in structure. T. Svensson found that the electrical conductivity of soln. of chromic sulphate slowly decreases in light.

The mol. electrical conductivity of the violet soln. has been determined by P. Walden, W. R. Whitney, A. Gubser, M. A. Graham, A. Colson, and H. C. Jones

and E. Mackay. L. G. Winston and H. C. Jones observed for violet soln., the mol. conductivity, $\mu$ mhos, for soln. of a mol of the salt in $v$ litres, and $\alpha$, the percentage ionization,

| | $v$ . . | 4 | 8 | 32 | 128 | 512 | 1024 | 4096 |
|---|---|---|---|---|---|---|---|---|
| $\mu$ | 0° . | 61·8 | 82·7 | 128·2 | 180·0 | 229·1 | 256 | 335·5 |
| | 12·5° . | 83·5 | 110·1 | 168·8 | 240·0 | 311·6 | 351·2 | 474 |
| | 25° . | 106·0 | 138·6 | 210·0 | 301·5 | 400·5 | 489 | 636 |
| | 35° . | 123·9 | 160·9 | 245·3 | 360·5 | 502·0 | 598 | 859 |
| $\alpha$ | 0° . | 18·4 | 24·7 | 38·2 | 53·6 | 68·3 | 76·2 | 100·0 |
| | 25° . | 16·6 | 21·7 | 33·0 | 47·4 | 62·8 | 76·8 | 100·0 |
| | 35° . | 14·4 | 18·7 | 28·5 | 41·9 | 58·5 | 69·5 | 100·0 |

E. J. Schaefer and H. C. Jones made observations at higher temp., but the results are affected by the change from the violet to the green sulphate between 40° and 50°. H. H. Hosford and H. C. Jones gave for a modified green soln. :

| $v$ . | 4 | 8 | 32 | 128 | 512 | 2048 |
|---|---|---|---|---|---|---|
| $\mu$ | 128·2 | 183·5 | 302·0 | 433·9 | 673·3 | 961·1 |
| | 160·0 | 227·8 | 354·4 | 522·7 | 811·1 | 1207·8 |
| | 189·6 | 262·9 | 417·4 | 606·0 | 977·3 | 1534·7 |

M. A. Graham gave for violet and the modified green soln. :

| $v$ . . | 16 | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|---|
| $\mu$ violet 0° | 85·37 | 100·0 | 117·7 | 139·2 | 166·6 | 194·2 | 232·2 |
| 25° | 151·5 | 177·1 | 211·8 | 255·0 | 310·2 | 379·5 | 476·9 |
| $\mu$ green 0° | 168·1 | 187·7 | 211·2 | 233·2 | 255·2 | 270·8 | 282·1 |
| 25° | 245·7 | 285·2 | 336·5 | 390·4 | 450·7 | 515·0 | 568·5 |

W. R. Whitney observed that the modified green soln. has a higher conductivity than the violet, thus, $\frac{1}{30}N$-$Cr_2(SO_4)_3$ has a sp. conductivity 0·001489 in the violet state at 25° and 0·001927 in the modified green state. He also found that the conductivity with the addition of increasing proportions of sodium or barium hydroxide decreases to a minimum and thereafter increases. With a $\frac{1}{30}N$-soln., at 25°, the minimum is reached when the added sodium hydroxide is eq. to $\frac{1}{6}$th of the total sulphate present, or when the added barium hydroxide is eq. to one-third the total sulphuric acid. Hence, it is assumed that one-sixth of the sulphate in the green soln. is present as free sulphuric acid, and one-third as $SO_4''$-ions. This is in agreement with A. Recoura's assumption that the formation of the green soln. is attended by the formation of the salt $[Cr_4O(SO_4)_4]SO_4$. A. W. Thomas and M. E. Baldwin studied the $H^{\cdot}$-ion conc. of soln. of chromic sulphate. During the passage of an electric current through a soln. of the violet sulphate, chromium passes to the cathode; but in a soln. of the modified salt, the hydrogen ions migrate to the cathode much more quickly. T. W. Richards and F. Bonnet, and H. G. Denham found that no chromium goes to the anode in a modified green soln. so that no complex acid-ions are formed. The basic complex in the modified soln. seems to carry only one positive charge and has a transport number of 41 when that of $SO_4''$ is 70. F. C. Thompson and W. R. Atkin suggested that the active agent in tanning with chromic sulphate soln. is a negatively charged chromium complex, but F. L. S. Jones found that electrophoresis experiments on normal and basic soln. of chromic chloride and sulphate and of chrome-alum showed that anodic migration of chromium occurs only in basic sulphate soln., and therefore no such negative complex can exist in soln. of the chloride or of chrome alum. The subject was studied by H. B. Merrill and J. G. Niedercorn. P. Philipp found the magnetic susceptibility ranged from $31·93\times10^{-6}$ mass units for soln. of sp. gr. 1·3453 to $33·04\times10^{-6}$ mass units for soln. of sp. gr. 1·03086. T. Ishiwara, and K. Honda and T. Ishiwara gave for the anhydrous salt $13·3\times10^{-6}$ at 15·7°, and $9·7\times10^{-6}$ mass units at 300°; and for the enneahydrate, $4·5\times10^{-6}$ mass units at 16·9°, and $7·4\times10^{-6}$ at 434·8°.

According to F. P. Venable and F. W. Miller both the violet and the green, modified soln. are acid towards indicators owing to the hydrolysis. A. Recoura

observed that distilling the aq. soln. furnishes an acidic distillate, while the dried salt does not lose acid at 100°. M. Krüger also found that alcohol poured over the green soln. takes up acid. F. P. Venable and F. W. Miller observed that eq. violet and green soln. required nearly the same amount of $\frac{1}{10}N$-$NH_4OH$ to produce the first appearance of a permanent precipitate. Their conclusion was that the two soln. must therefore contain nearly the same proportion of acid, but as W. R. Whitney pointed out, the conclusion is wrong because alkali and ammonium hydroxides or carbonate turn the violet soln. green, and this change in colour precedes the formation of the permanent precipitate. C. R. C. Tichborne observed that if a soln. of chromic sulphate be heated to 177° under press. for 2 to 3 hrs., a precipitate of a basic sulphate is formed. G. Powarnin found that in dil. soln., chromium sulphate is more strongly hydrolyzed than aluminium sulphate; and that the hydrolysis is decreased in the presence of $SO_4''$-ions or $Cl'$-ions, and also by alcohol and formaldehyde. Many others have observed the hydrolysis of soln. of chromic sulphate. H. G. Denham measured the e.m.f., $E$, (H zero) of the cell $H_2 \mid Cr_2(SO_4)_{3\,violet}, NH_4NO_3 \mid$ calomel electrode, and calculated the $H'$-ion conc., $[H']$, and the percentage hydrolysis, $x$, as well as the ionization constant, $K$, where $K_1=[Cr(SO_4)(OH)][H']/[Cr(SO_4)']$, obtained from the hydrolytic reactions: $Cr_2(SO_4)_3+2H_2O \rightleftharpoons 2Cr(SO_4)OH+H_2SO_4$, or $Cr(SO_4)'+H_2O \rightleftharpoons Cr(SO_4)(OH)+H'$, for soln. of a mol of $Cr_2(SO_4)_3$ in $v$ litres, at 25°,

| $v$ | 6 | 8 | 16 | 32 | 64 | 128 |
|---|---|---|---|---|---|---|
| $E$ | −0·1417 | −0·1444 | −0·1533 | −0·1604 | −0·1713 | −0·1653 |
| $[H'] \times 10^2$ | 0·396 | 0·357 | 0·252 | 0·191 | 0·125 | 0·158 |
| $x$ | 1·19 | 1·42 | 2·02 | 3·05 | 4·00 | 10·10 |
| $K_1 \times 10^4$ | 0·24 | 0·26 | 0·26 | 0·30 | 0·26 | 0·88 |

The great increase in the ionization constant with high dilution is taken to mean that another stage in the progressive hydrolysis occurs, namely, $Cr_2(SO_4)''''+4H_2O \rightleftharpoons Cr_2(SO_4)(OH)_4+4H'$, for which he found that $K_2=[H']^4[Cr_2(SO_4)(OH)_4]\text{-}[Cr_2(SO_4)'''']$, or $K_2=0{\cdot}129\times10^{-14}$. H. M. Vernon estimated the degree of ionization from the colour. M. A. Graham calculated from the conductivity of the violet soln. that the percentage hydrolysis is :

| $v$ | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|
| $x$ | 1·78 | 3·19 | 4·76 | 8·08 | 16·24 | 33·98 |

At 0°, the violet soln. is only slightly hydrolyzed. The hydrolysis calculated from the effect on the velocity of inversion of cane sugar shows that the change from violet to green is much more rapid than the reverse process. A. Recoura found from the thermal data that in the modified green $\frac{1}{12}N$-soln., about one-sixth of the total sulphuric acid is free; and W. R. Whitney observed the effect of soln. of chromic sulphate on the hydrolysis of methyl acetate, and concluded that the green soln. possesses a hydrolyzing power equal to that of a mixture of one-sixth the eq. of free acid, with the corresponding amounts of the violet salt. The effects on the rate of inversion of cane sugar were too complex to enable a calculation to be made of the degree of hydrolysis of the soln. H. G. Denham calculated data for green modified soln. as in the case above cited for violet soln. and found

| $v$ | 6 | 8 | 16 | 32 | 64 | 128 |
|---|---|---|---|---|---|---|
| $E$ | −0·0528 | −0·0589 | −0·0740 | −0·0871 | −0·0968 | −0·1095 |
| $[H']$ | 0·1236 | 0·1005 | 0·05572 | 0·03342 | 0·02286 | 0·01393 |
| $x$ | 37·1 | 40·2 | 44·6 | 53·4 | 72·9 | 88·8 |
| $K_1$ | 0·18 | 0·21 | 0·23 | — | — | — |

The value of $x$ is calculated on the assumption that the reaction is $[Cr_4(SO_4)_4](SO_4)_2+4H_2O \rightleftharpoons 2H_2SO_4+[Cr_4(SO_4)_4](OH)_4$; and $K_1$ is calculated for the formation of $[Cr_4(SO_4)_4](SO_4)(OH)_2$. As in the case of the violet soln., M. A. Graham calculated for the hydrolysis of the green modified soln., by the conductivity method,

| $v$ | 16 | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|---|
| $x$ | 17·02 | 22·04 | 27·68 | 33·42 | 40·74 | 51·10 | 60·49 |

In both cases M. A. Graham's results are lower than those of H. G. Denham. The hydrolyses calculated from the effect on the inversion of cane sugar for soln. with $v=5$ and 10, are respectively 8·39 and 6·84 per cent., but the results are not so trustworthy. H. T. S. Britton calculated that a violet 0·0050$M$-soln. of chromic sulphate was hydrolyzed to the extent of 2·16 per cent., and a green 0·0067$M$-soln., 28·7 per cent. The electrometric titration curve is shown in Fig. 79. W. J. Chater and J. S. Mudd found a change in the $p_H$ value at 2·3 and basicity 124. T. Svensson observed that a cell of chromic sulphate soln. gives an increased e.m.f. when illuminated. The change owing to the presence of neutral salt is dependent on the basicity. The difference in acidity caused by the neutral salt is a minimum at basicity 124. N. Demassieux and J. Heyrovsky obtained analogous polarization curves with chromic sulphates as were obtained with the chlorides (*q.v.*).

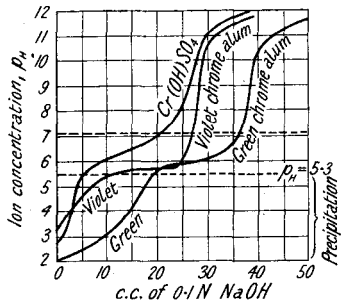


FIG. 79.—The Electrometric Titration Curves of Chromic Sulphate Solutions.

The penetration of gelatin jelly by chromium sulphate soln. is greater the greater the acidity. From his observations of the physical properties of the soln., and on those of T. W. Richards and F. Bonnet, H. G. Denham inferred that when the violet soln. is heated, the salt undergoes hydrolysis in the ordinary way; it is assumed that two mols. of the salt unite to form a complex: $2Cr_2(SO_4)_3=[Cr_4(SO_4)_4](SO_4)_2$, and that the complex then hydrolyzes: $[Cr_4(SO_4)_4](SO_4)_2+2H_2O\rightleftharpoons[Cr_4(SO_4)_4]SO_4(OH)_2+H_2SO_4$ with up to $\frac{1}{40}M$-soln., and on further dilution: $[Cr_4(SO_4)_4](SO_4)_2+4H_2O=2H_2SO_4+[Cr_4(SO_4)_4(OH)_4]$. D. M. Yost studied the rate of oxidation of soln. of chromic sulphate by potassium persulphate (*q.v.*). F. Hans found that chromic salts and silver salts (if soluble enough) react in accord with $Cr_2O_3+3Ag_2O=2CrO_3+6Ag$. J. Poizat studied the action of chromic sulphate on the decomposition of hydrogen dioxide. W. R. Hodgkinson and C. C. Trench observed that chromium sulphate is reduced to a mixture of oxide and sulphide when heated in ammonia. F. Feigl found that a boiling soln. of chromic sulphate in alkali-lye is oxidized to chromate by charcoal (with oxygen in the pores); and G. Fuseya and co-workers discussed the formation of complex cations with chromic sulphate and glycine. W. Manchot and co-workers showed that soln. with 22·356 and 44·712 grms. $Cr_2(SO_4)_3$ per 100 c.c. dissolve respectively 31·8 and 18·2 c.c. of nitrous oxide per 100 c.c. of soln., and respectively 56·7 and 32·4 c.c. of acetylene.

L. N. Vauquelin, J. J. Berzelius, A. Schrötter, M. Siewert, H. Schiff, R. Bunsen, and C. R. C. Tichborne obtained precipitates of basic salts by the action of water on soln. of chromic hydroxide in sulphuric acid. In some cases the composition of the product approximated to $3Cr_2O_3.2SO_3$; H. Schiff obtained one approximating $3Cr_2O_3.4SO_3.12H_2O$; and M. Siewert, precipitates approximating to $5Cr_2O_3.8SO_3$, and to $5Cr_2O_3.12SO_3$. There is nothing to show that these products are anything more than arbitrary stages in the progressive hydrolysis of chromic sulphate. H. Schiff also obtained **chromic dioxysulphate,** $Cr_2O_2SO_4.nH_2O$, by dissolving a precipitated basic salt in dil. hydrochloric acid, and after diluting the soln., boiling it for some hours. A. Werner regarded it as **chromic dihydroxytetraquosulphate,** $[Cr(OH)_2(H_2O)_4]_2SO_4$, and obtained it by adding 10 grms. of pyridine to a soln. of 20 grms. of chrome-alum and 30 grms. of sodium sulphate in 300 grms. of water. The pale green, silky needles are but slightly soluble in water, and with organic and mineral acids form hexaquo-salts of the type $[Cr(H_2O)_6]X_3$. O. Grimm's observations on the chlorides are also applicable here.

A. Schrötter found that when dil. sulphuric acid sat. with hydrated chromic oxide is boiled for a long time and concentrated it furnishes a green soln. which is acidic to test-paper, and leaves on drying a green, amorphous mass from which

the whole of the sulphate is expelled by ignition. H. Schiff added that at 100°, four mols. of water are given off and at a higher temp., one mol. A. Schrötter gave the formula of the compound dried at 50° to 60°, $2Cr(OH)SO_4.4H_2O$, but H. Schiff, in agreement with H. Löwel, gave $Cr_2(OH)_4SO_4.4H_2O$, **chromic tetrahydroxysulphate**. A. Schrötter found that a soln. of the salt appears ruby-red viewed by transmitted sunlight, or candle-light; and H. F. Talbot added that if the soln. which appears green by day-light, and red by candle-light be introduced into a prism with a refracting angle of 5° or 10°, and then placed between the eye and the candle-flame, red and blue images of the candle appear, and the rest of the visible spectrum is absorbed so that a kind of double refraction is produced. If the soln. be placed in a bottle and viewed by transmitted light, the two images overlap, the green predominates by daylight, and the red, by candle-light. A conc. soln. of the sulphate is rendered turbid by the addition of water, depositing the more basic 3 : 2-sulphate, and becoming paler in proportion to the amount of water added. On evaporation, however, the precipitate redissolves—when the dil. soln. filtered from the precipitate is heated, it deposits more of the 3 : 2-sulphate, which again disappears on boiling. A soln. of sp. gr. 1·219 and upwards deposits nothing when heated; a soln. of sp. gr. 1·166 becomes turbid at 57°; a soln. of sp. gr. 1·037—1·031, at 64°; one of sp. gr. 1·002, at 45°; and one of sp. gr. 1·001, at 55°; while still more dil. soln. remain clear when boiled. According to H. Löwel, if the green soln. be treated with as much acid as it already contains, ammonia then produces a dark green precipitate which is only slightly soluble in ammonia. M. Siewert found that when soln. of the violet salt is boiled with an excess of hydrated chromic oxide, and the green soln. evaporated almost to the point of solidification, it becomes turbid when water is added, but clarifies again on evaporation. Absolute alcohol precipitates from the soln. a green syrup of the 1 : 2-sulphate, and it forms a clear soln. with water. The soln. does not become turbid when boiled, but gives the 1 : 2-sulphate as a precipitate when alcohol is added. B. Cabrera and S. P. de Rubies studied the magnetic qualities of green and violet **chromic oxydisulphate,** $Cr_2O(SO_4)_2.nH_2O$, and found that they change when the soln. is kept for some time. It is suggested that this is due to the changes: $[Cr_2(SO_4)_2O] \rightarrow [Cr_2(SO_4)O]SO_4 \rightarrow [Cr_2O](SO_4)_2$. According to L. and P. Wöhler and W. Plüddemann, the oxydisulphate, obtained by heating the basic sulphate to 280° in a current of carbon dioxide, has a dissociation press. of 91 mm. at 340°, and 191 mm. at 372°; and the heat of dissociation is 21·97 Cals. Likewise, **chromic trioxytrisulphate,** $Cr_4O_3(SO_4)_3$, obtained by heating the basic sulphate to 450° or 460° in a current of carbon dioxide, has a dissociation press. of 146 mm. at 640°, and 400 mm. at 660°; the heat of dissociation is 61·62 Cals.

According to A. Colson, **chromic oxypentasulphate,** $Cr_4O(SO_4)_5.nH_2O$, with *two masked $SO_4$-radicles* is obtained by treating a cold soln. of 100 grms. of chrome-alum in 4 litres of water of ammonia; digesting an excess of the washed precipitate in sulphuric acid; and evaporating the soln. in vacuo. Only three of the five sulphate radicles are precipitated from a soln. of the salt by barium chloride. The salt in alcoholic soln. has the same composition as the solid. If the soln. of this salt is slowly crystallized, by evaporation in dry air, it yields the oxypentasulphate, $Cr_4O(SO_4)_5.12H_2O$, with *three masked $SO_4$-radicles*. A. Colson said that when a soln. of the violet sulphate is heated, it forms the oxypentasulphate, $HSO_4(CrSO_4)_2.O.(CrSO_4)_2.O.CrSO_4$, in which there are *four masked $SO_4$-radicles*. If the soln. is boiled and suddenly cooled, it yields the sulphate with all its sulphate radicles masked.

According to P. Nicolardot, when a violet soln. is boiled, and the resulting green liquor is heated with barium sulphate, part of the sulphuric acid is precipitated, and when the filtrate is allowed to evaporate spontaneously, there remains chromic oxypentasulphate, $Cr_2O_3.2{\cdot}5SO_3.7{\cdot}5H_2O$, that is, $Cr_4O(SO_4)_5.15H_2O$, with *all five $SO_4$-radicles masked*. This salt appears as a non-crystalline solid, readily soluble in water to form a green soln., but insoluble in alcohol or acetone, and precipitated

from aq. soln. by these liquids. Soln. of the salt do not yield precipitates with barium chloride or with sodium phosphate; it differs in this respect from the sulphate of sulphochromyl hydroxide described, but not isolated, by A. Recoura. According to A. Colson, the equilibrium indicated in the following equation, $2Cr_2(SO_4)_3+H_2O \rightleftharpoons H_2SO_4+Cr_4O(SO_4)_5$, is only relatively stable, and the penta-sulphate, $Cr_4O(SO_4)_5$, is acted on by boiling water with momentary production of a fresh quantity of acid, thus: $Cr_4O(SO_4)_5+H_2O \rightleftharpoons Cr_4O_2(SO_4)_4+H_2SO_4$. This is proved by the repeated boiling of a 0·1*N*-soln. of the normal green sulphate, $Cr_2(SO_4)_3.10H_2O$, cooling very rapidly, and then adding baryta-soln. The amount of heat developed in the reaction shows that each successive boiling after the first liberates sulphuric acid according to the second equation.

C. F. Cross and A. F. Higgin obtained an acid salt approximating $4Cr_2O_3.6SO_3.7H_2SO_4$, by heating chromic oxide with conc. sulphuric acid. The grey powder is insoluble in water, and is attacked with difficulty by alkali-lye. According to M. Traube, and A. Schrötter, a pale puce or grey powder is formed when a green mush of conc. sulphuric acid and a basic chromic sulphate or hydrated oxide is heated until sulphuric acid begins to volatilize: if a large proportion of sulphuric acid is employed, a green soln. is obtained, which when heated becomes colourless, and deposits the puce or grey powder. The product is washed with water and dried. A. Schrötter regarded it as the normal sulphate, but M. Traube, and M. Siewert showed that it is rather **chromic dihydroheptasulphate,** $2Cr_2(SO_4)_3.H_2SO_4$. A. Étard supposed the compound to be constituted $Cr_2(SO_4)_6Cr_2.H_2SO_4$, or $HSO_4.Cr_2(SO_4)_5Cr_2.HSO_4$; and G. N. Wyrouboff, $[Cr_2O_3(SO_2)_4O_4Cr_2O_3(SO_2)_3O_2(OH)_2]_3$. M. Traube also obtained the same salt contaminated with some potassium salt by the action of conc. sulphuric acid on potassium dichromate and chrome-alum; and T. Klobb, by the action of the acid on the ammonium chromic sulphate. M. Traube said that the powder is sometimes so fine that it will pass through filter-paper; and will remain suspended in water a considerable time, but can be rapidly precipitated by the addition of various salts—*e.g.* ammonium carbonate, potassium sulphate, etc. The powder appears grey by daylight, and green by candle-light; and A. Schrötter said that the powder may appear a very light red by diffused daylight; pale green by sunlight; and verdigris-green by candle-light. Every time it is heated, it appears puce-coloured. When heated to redness, it gives off all its sulphuric acid; and, according to M. Traube, a pyrophoric mixture of chromic sulphide and oxide may be formed. When heated in hydrogen it yields water, hydrogen sulphide, sulphur, and chromic oxide; while a current of hydrogen sulphide converts the heated salt into black chromic sulphide, with the formation of water, sulphur, and sulphur dioxide. It is insoluble in cold water, but when boiled for a long time with water, or when allowed to stand for a long time in contact with water, some of it passes into soln. It is insoluble in aq. ammonia and in strong mineral acids—*e.g.* hydrochloric, sulphuric, and nitric acids, or in aqua regia. The salt is readily decomposed by fused alkali hydroxide, or by a boiling soln. of the hydroxide or carbonate.

R. F. Weinland and R. Krebs prepared **chromic dihydrotetrasulphate,** $Cr_2(SO_4)_3.H_2SO_4.nH_2O$, by the action of an excess of conc. sulphuric acid on a soln. of chrome-alum. The *hexadecahydrate* separates in the *violet form* if the mixture is made with well-cooled liquids; columnar crystals separate from a soln. of 100 mols of sulphuric acid and one of chrome-alum when evaporated in vacuo, while if the mixture is made with warm soln., the *green form* is produced in acicular crystals. Only with the violet soln. is all the sulphuric acid precipitated by barium chloride. The salt loses no water if the salt be kept over sulphuric acid in vacuo. A soln. of a mol of the violet sulphate in 124·7 litres of water has a conductivity of 116, and this value does not change with time; on the other hand, a soln. of the green salt of nearly the same conc. has a conductivity of 76·5 which in 2 hrs. rises to 80·8, in 5 hrs to 93·2, and in 24 hrs. to 101·8. It is therefore inferred that the

violet salt is to be formulated $[Cr_2(H_2O)_{16}](SO_4)_3(H_2SO_4)$, and that with the green salt, some sulphate is contained within the co-ordinated group. If the original components interact at —15°, long, tabular, violet crystals of the *tetracosihydrate* are formed, $[Cr_2(H_2O)_{16}](SO_4)_3(H_2SO_4).8H_2O$, or $[Cr(H_2O)_8](SO_4(HSO_4).4H_2O$. This salt can be regarded as being related to chrome-alum since both contain the same number of water mols., and in both the sulphate-radicle is all precipitated by barium sulphate: $HCr(SO_4)_2.12H_2O$, and $KCr(SO_4)_2.12H_2O$. Chrome-alum loses 6 mols. of water over sulphuric acid in vacuo, while hydrochromodisulphuric acid loses 4 mols., yielding the hexadecahydrate. Still further, if 140 mols of sulphuric acid be employed to one mol of sulphate, **chromic tetrahydropentasulphate,** $Cr_2(SO_4)_3.2H_2SO_4.18H_2O$, or $[Cr_2(H_2O)_{18}](SO_4)_3(H_2SO_4)_2$, is formed in rectangular plates. This *violet form* of the salt becomes greyish-green when heated to 100°, with the loss of some water. Barium chloride does not precipitate all the sulphate from the green aq. soln., but it does so from the violet soln. Consequently, some sulphate radicle is contained within the co-ordination group of the green salt.

According to A. Recoura, green chromic sulphate can unite with one, two, and three mols. of sulphuric acid, or metal sulphates to form complex **chromisulphuric acids,** or their salts. The acids are prepared by evaporating to dryness on a water-bath a soln. of a mol of green chromic sulphate with one, two, or three mols of sulphuric acid, and heating the green product for a long time to 110° to 120°. No sulphate is precipitated when barium chloride is first added to aq. soln. of the acids. There are thus obtained **chromitetrasulphuric acid,** $Cr_2(SO_4)_3.H_2SO_4.nH_2O$, or $H_2[Cr_2(SO_4)_4]nH_2O$, or, according to W. R. Whitney, $[Cr_2(H_2O)_4(SO_4)]H_2$; **chromipentasulphuric acid,** $Cr_2(SO_4)_3.2H_2SO_4.nH_2O$, or $H_4[Cr_2(SO_4)_5].nH_2O$, or, according to W. R. Whitney, $[Cr_2(H_2O)_2(SO_4)_5]H_4$; and **chromihexasulphuric acid,** $Cr_2(SO_4)_3.3H_2SO_4.nH_2O$, or $H_6[Cr(SO_4)_6].nH_2O$, or, according to W. R. Whitney, $[Cr(SO_4)_6]H_6$. G. N. Wyrouboff regarded these acids as esters of the green sulphate in which two hydroxyl radicles are replaced by chromosulphuric acid. These acids are accordingly represented respectively by $[Cr_2O(OH)_4(SO_2)_4]O(OH)_6$; by $[Cr_2O(OH)_4(SO_2)_5]O_2(OH)_6$; and by $[Cr_2O(OH)_4(SO_2)_6]O_3(OH)_6$. According to A. Recoura, the proportion of contained water is dependent on the duration of the heating at 110° to 120°, and they lose no sulphuric acid below 170°. E. Moles and M. Crespi gave for the sp. gr. of the acid $HCr(SO_4)_2$, 2·724 at 25°/4°, and 90·5 for the mol. vol.; for the acid $HCr(SO_4.H_2O)_2$, they found the sp. gr. 2·516, and the mol. vol. 111·5; and for $H[Cr(H_2O)_6](SO_4.H_2O)_2$, respectively 2·009 and 195. They also observed that the acid $H[Cr(H_2O)_6](SO_4.H_2O)_2$ loses 6·03 mols. of water at 120°, and $HCr(SO_4.H_2O)_2$, 1·91 mols. at 350°. According to A. Recoura, the acids are stable when dry, and they are freely soluble in water forming green soln. The basicity of the acids just indicated accords with the thermal values of the neutralization of soln. of the respective acids with 2, 4, and 6 mols. of a soln. of sodium hydroxide—one mol per 20 litres: $(H_2[Cr_2(SO_4)_4],2NaOH)=33·3$ Cals.; $(H_4[Cr(SO_4)_5],4NaOH)=2\times33$ Cals.; and $(H_6[Cr(SO_4)_6],6NaOH)=3\times32$ Cals. When $(H_2SO_4,2NaOH)=30·8$ Cals. under similar conditions. The formulæ are also in accord with the fact that freshly prepared soln. do not show the reactions of chromium or sulphates with mild reagents like sodium phosphate and barium chloride. In course of time, particularly when heated, or when treated with stronger reagents like sodium hydroxide, the soln. do give the reactions of chromium and of sulphuric acid. W. R. Whitney found the electrical conductivity, $\lambda$ mhos, of soln. a gram-equivalent in $v$ litres at 0° to be close to the values for sulphuric acid of the same conc.,

| $v$ | . . . . . | 202 | 404 | 808 | 1616 | 3232 |
|---|---|---|---|---|---|---|
| $\lambda$ | $\frac{1}{2}H_2SO_4$ . . . | 210·7 | 223·7 | 236·0 | 245·5 | 249·2 |
| | $\frac{1}{2}H_2[Cr_2(SO_4)_3(H_2SO_4)]$ | 210·6 | 223·1 | 232·5 | 241·0 | 250·9 |
| | $\frac{1}{4}H_4[Cr_2(SO_4)_3(H_2SO_4)_2]$ | 210·9 | 222·9 | 231·5 | 240·6 | 260·5 |
| | $\frac{1}{6}H_6[Cr_2(SO_4)_3(H_2SO_4)_3]$ | 210·7 | 222·3 | 236·0 | 244·0 | 250·8 |

Consequently, W. R. Whitney inferred that the ionization, the velocities of transport

of the anions, and the strengths of the four acids are approximately the same; similar conclusions were drawn from the action of the four acids on the hydrolysis of methyl acetate. Determinations of the f.p. show that the number of molecules in soln. of these acids is conditioned by the free sulphuric acid present in the soln. The f.p. of sulphuric acid is the same as that of one of these acids with the same content of free sulphuric acid—*i.e.* acid not bound to the chromium. Hence, chromic sulphate does not act as individual compound, but it forms complexes in agreement with the results deduced from the chemical behaviour of the complexes. When the soln. are kept for some time, the f.p. data show that there is an increase in the number of molecules. For an isomeric form of chromic tetrasulphuric acid, *vide infra.*

A. Recoura attempted to prepare chromisulphuric acids with more than three mols of sulphuric acid per mol. of chromic sulphate, but found that the products have quite a different character. Thus, when a soln. of a mol of the green sulphate with 4, 5, or 6 mols. of sulphuric acid is evaporated on a water-bath, and the resulting dark green syrup is heated for some days at 115°, **chromipolysulphuric acids**—respectively **chromiheptasulphuric acid,** $Cr_2(SO_4)_3.4H_2SO_4$; **chromioctosulphuric acid,** $Cr_2(SO_4)_3.5H_2SO_4$; and **chromiennea-sulphuric acid,** $Cr_2(SO_4)_3.6H_2SO_4$—are obtained in the form of transparent, green glasses which form yellowish-green soln. with water. These soln. form transparent, gelatinous masses after standing a few days; they are coagulated at 100°; on the addition of strong acids they furnish green flecks; and they give green, insoluble, flocculent precipitates when treated with soln. of the salts of the metals. In this reaction the complex is reduced to a chromitetrasulphate, $MSO_4.Cr_2(SO_4)_3$ or $Cr(SO_3)_4O_2(OH)_2$ and the excess sulphate is set free as sulphuric acid; thus, chromiheptasulphuric acid reacts with cupric chloride: $[Cr_2(SO_4)_3(H_2SO_4)_4]+CuCl_2=3H_2SO_4+2HCl+[Cr_2(SO_4)_4]Cu$. A. Recoura also prepared the chromitetrasulphuric acid by heating chromiheptasulphuric acid to 140°–150° until it no longer loses weight, and has lost 3 mols. of sulphuric acid. The grey powder is an isomeric form of the chromitetrasulphuric acid indicated above. It forms a greenish-yellow, opalescent or colloidal soln. with water, and with soln. of the metal salts, insoluble chromi-tetrasulphates. Chromitetrasulphuric acid, $Cr_2O_2(SO_3)_4(OH)_2$, or $[Cr_2(SO_4)_4]H_2$, is dibasic, and it is a stronger acid than sulphuric acid. Strong acids precipitate it as a gelatinous mass from soln. of its salts. The acid can be transformed into its isomeric form by boiling with water; and with boiling alkali-lye, chromites are formed. G. N. Wyrouboff believed that these chromipolysulphuric acids are not chemical individuals, but mixtures of sulphuric acid with the chromitetrasulphuric acid.

A. Recoura showed that the green chromic sulphate can unite with one, two, or three mols. of chromic acid to form **chromitrisulphatochromic acids.** These are analogous to the chromisulphuric acids. Thus, there is **chromitrisulphato-chromic acid,** $Cr_2(SO_4)_3.H_2CrO_4$, or $H_2[Cr_2(SO_4)_3(CrO_4)]$; **chromitrisulphatodi-chromic acid,** $Cr_2(SO_4)_3.2H_2CrO_4$, or $H_4[Cr_2(SO_4)_3(CrO_4)_2]$; and **chromitrisulphato-trichromic acid,** $Cr_2(SO_4)_3.3H_2CrO_4$, or $H_6[Cr_2(SO_4)_3(CrO_4)_3]$. The constitutions may also be represented respectively by the formulæ:

These acids form dark brown amorphous masses which, in freshly prepared, dil. soln. exhibit the characteristic reactions of neither $SO_4''$—nor $CrO_4''$—radicles, slowly decompose when they do show the reactions of these radicles. Arguing by analogy, and from some observations on the heats of neutralization, it is inferred that the constitution of the chromisulphatochromic acids resembles that of the chromisulphuric acids. If the alkali chromates are employed in place of chromic acid in the preparation of these products then the corresponding chromisulphatochromates are formed. J. Poizat studied the action of chromi-mono-, -di-, and tri-sulphuric acids on hydrogen dioxide.

According to G. N. Wyrouboff, when an aq. soln. of chromisulphuric acid is heated, a coagulum is formed which he called *chromium sulphochromate*, $[Cr_2O_2(OH)_4(SO_2)_4O_2(OH)_2]Cr_2(OH)_6$, and which is identical with that obtained by precipi-tating a violet salt of chromium in the cold with sulphochromic acid. If this is maintained for

some time in contact with boiling water, it becomes hydrated, dissolves slowly, and finally passes entirely into a soln. of the green sulphate. Chromium sulphochromate, when heated at 120°, becomes soluble in water and the soln. yields insoluble precipitates with metallic salts, *chromosulphochromates* being formed. When chromium sulphochromate is treated with hydrochloric acid, what he called *chromosulphochromic acid*, $[Cr_2O_2(OH)_4(SO_2)_4O_3.Cr_2O(OH)_2(SO_2)_3(OH_6)][(OH)_2$, is precipitated as a dark green, gelatinous mass which dissolves in water, yielding an opalescent soln. On adding 2 mols of sulphuric acid and a little water to 1 mol of chromium sulphochromate, evaporating on the water-bath, and heating for some hours at 120°, *chromodisulphochromic acid*, $[Cr_2O_2(OH)_4(SO_2)_4O_3]_2Cr_2O(OH)_2(SO_2)_3(OH)_4(OH)_4.H_2O$, is obtained, which yields an insoluble salt with iron. With sulphochromic acid, chromium sulphochromate yields a chromosulphodichromate. If chromium sulphate is heated with an excess of sulphuric acid to a temp. not exceeding 150°, a clear green, gelatinous precipitate of sulphochromic acid is formed; on continuing the heating and at the same time allowing the temp. to rise, the green precipitate gradually changes into a heavy, greyish-yellow powder, soluble in water, yielding a milky, strongly acid soln. The same substance is obtained by heating sulphochromic acid for some time at 250°, and is the first anhydride of a polymeride of chromosulphochromic acid. Although sulphochromic acid forms insoluble compounds with the metals, it does not give precipitates with all the salts of the metals. Thus, it gives a precipitate with a soln. of mercuric nitrate or acetate, but not with mercuric bromide. This is explained by saying that the last-named salt is an anhydride and not a normal salt.

The products obtained by J. L. Gay Lussac [3] by the action of sulphuric acid on chromic anhydride, were shown by J. Fritzsche, and P. Plantamour to be mechanical mixtures. J. Meyer and V. Stateczny found the f.p. of mixtures of chromic acid and water-free $H_2SO_4$ to be:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $CrO_3$ . | 0 | 0·16 | 1·2 | 2·02 | 3·13 | 4·17 | 5·37 | 8·66 per cent. |
| F.p. . | 10·45° | 10·2° | 8·6° | 5·8° | 7·6° | 8·8° | 9·6° | 9·8° |

The eutectic at 5·5° corresponds with 2·2 per cent. $CrO_3$. A. W. Rakowsky and D. N. Tarassenkoff found that the compound decomposes at ordinary temp. with a marked change of colour when the humidity exceeds 1·7 per cent. W. Ipatieff and A. Kisseleff obtained **potassium trisulphatodichromate,** $2KCrO_4.Cr_2(SO_4)_3.H_2O$, by the action of hydrogen under press. on a soln. of potassium dichromate (*q.v.*). P. A. Bolley added chromium trioxide to conc. sulphuric acid, until no more dissolved, the resulting dark brown oil forms a pale brown, granular mass in a few days. A. Schrötter obtained a yellowish-brown substance to which he gave the formula $CrO_3.3SO_3$; and A. Pictet and G. Karl heated a mixture of sulphur and chromium trioxides in a sealed tube and obtained a yellowish-brown mass of $CrO_3.SO_3$, sometimes regarded as **chromyl sulphate,** $CrO_2(SO_4)$. The products are unstable in air, and liberate chromium trioxide by the action of moisture. The observations of L. F. Gilbert and co-workers, and A. W. Rakowsky and D. N. Tarassenkoff on the solubility of chromium trioxide in soln. of sulphur trioxide at 25° and 45° were discussed in connection with chromium trioxide. The results of L. F. Gilbert and co-workers are shown graphically in Fig. 80, for the ternary system: $CrO_3$–$SO_3$–$H_2O$ at 25°. There are three solid phases $CrO_3$; $CrO_3.SO_3$; and what is thought to be the *monohydrate*, $CrO_3.SO_3.H_2O$. Chromyl sulphate is usually brown and minutely crystalline, and sometimes amorphous; the hydrate is also amorphous. Both compounds are very hygroscopic, and liberate scarlet chromium trioxide on exposure to air.

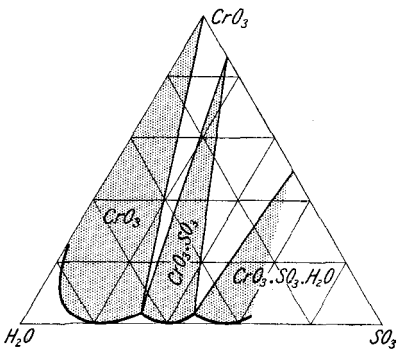


FIG. 80.—The Ternary System: $CrO_3$–$SO_3$–$H_2O$ at 25°.

J. Meyer and V. Stateczny said that the orange precipitate which gradually forms from soln. of chromium trioxide in 95 to 100 per cent. $H_2SO_4$ is **chromatosulphuric acid,** $H_2CrSO_7$, or $H_2[CrO_3(SO_4)]$, and that it appears as a dark orange

powder which reacts very energetically with water to form a brick-red soln. of chromic and sulphuric acids. The acid can be preserved over phosphorus pentoxide, or in a sealed tube. It is decomposed in light. It is insoluble in carbon disulphide and similar liquids; it is gradually reduced by ether, ligroin, and benzene. It darkens in colour when heated, it sinters at 168°–170°, and at 190° forms a blood-red liquid and then decomposes with the evolution of oxygen. It is a powerful oxidizing agent—a drop of alcohol is inflamed by the acid; and it forms chromic oxide with the evolution of sulphur dioxide when treated with aldehyde. Naphthalene, and phenol are carbonized; anthracene yields acetic acid; and a mixture of sugar and potassium chlorate is exploded by the acid. It does not form salts by direct neutralization. H. Schiff prepared **potassium chromatosulphate,** $K_2CrSO_7$, or $K_2[CrO_3(SO_4)]$, by melting potassium sulphate or hydrosulphate with potassium chlorochromate; and J. Meyer and V. Stateczny, by the reaction $K_2Cr_2O_7+2KHSO_4=H_2O+2K_2CrSO_7$. They also prepared **ammonium chromatosulphate,** $(NH_4)_2[CrO_3(SO_4)]$, and **sodium chromatosulphate,** $Na_2[CrO_3(SO_4)]$, in a similar manner. By heating a mixture of barium chromate and sulphur trioxide in a sealed tube for 3 hrs. at 120°, **barium chromatosulphate,** $Ba[CrO_3(SO_4)]$, was obtained; and **strontium chromatosulphate,** $Sr[CrO_3(SO_4)]$, by heating to 160° for 3 hrs. a mixture of strontium sulphate and chromium trioxide; and similarly with **calcium chromatosulphate,** $Ca[CrO_3(SO_4)]$. B. Cabrera and S. P. de Rubies studied the magnetic properties of the products formed by the addition of sulphuric acid to the oxychromic salts.

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## § 30. The Complex Salts of Chromic Sulphates

The most important complex sulphates are the chrome-alums in which tervalent chromium replaces aluminium in the ordinary alums, so that the general formula for the series is $R'_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $R'Cr(SO_4)_2.12H_2O$. A. Mitscherlich [1] prepared **ammonium chromium sulphate,** or **ammonium disulphatochromiate,** $(NH_4)_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $(NH_4)Cr(SO_4)_2.12H_2O$, by mixing a sulphuric acid soln. of violet chromic sulphate with ammonia; A. Schrötter, by adding ammonium sulphate to a conc. soln. of violet chromic sulphate when crystals of the ammonium chrome-alum are precipitated, and J. L. Howe and E. A. O'Neal, by the electrolysis of a soln. of ammonium chromate in sulphuric acid—this salt collects at the negative pole. J. Hertkorn prepared it as in the case of the potassium salt—*vide infra*. A. Mitscherlich found that the crystals are regular octahedra, with surfaces of cubes and dodecahedra. The cleavage on the octahedral face is indistinct. T. Klobb prepared solid soln. of ammonium chromic alum with ammonium ferric and with ammonium aluminium alums. W. Haidinger found the crystals to be violet-blue passing into columbine-red; and, added A. Schrötter, they are ruby-red by transmitted light. They are moderately transparent, and have a sweetish saline taste. A. Schrötter gave 1·736 for the sp. gr. at 21°; O. Pettersson, 1·728 at 20°; and J. H. Gladstone, 1·719. G. T. Gerlach found the sp. gr. of violet soln. containing 2·195, 4·390, and 6·585 per cent. $(NH_4)Cr(SO_4)_2$ are respectively 1·0200, 1·0405, and 1·0610 at 15°/15°; and with green soln. at 15°/15°,

| $(NH_4)Cr(SO_4)_2$ | 5·487 | 10·974 | 16·461 | 27·435 | 38·409 | 49·383 per cent. |
|---|---|---|---|---|---|---|
| Sp. gr. . . | 1·044 | 1·091 | 1·142 | 1·255 | 1·384 | 1·532 |

The sp. gr. of the sat. violet soln. is 1·070 at 15°/15°. P. A. Favre and C. A. Valson studied the change in vol. which occurs when this alum passes into soln. H. C. Jones and E. Mackay found the lowerings of the f.p. produced by ammonium chrome alum for 0·097, 0·0484, and 0·0291 per cent. soln. are, respectively, 7·92, 8·26, and 9·14, and these values are about 0·8 less than the sum of the values of the constituents. This means that the f.p. of the soln. confirm the evidence from the conductivity data, that alum molecules exist to some extent in the more conc. soln. According to A. Schrötter, the salt effloresces superficially in air, and becomes covered with a pearl-grey powder. The m.p. is 100°. J. Locke gave 94° for the m.p. A. Schrötter observed that three-fourths of the water of crystallization is evolved when the salt melts, and the liquid shows no signs of dichroism; it solidifies to a pale green mass which gives off its remaining water above 300°. G. D. van Cleeff said that half its combined water is lost over sulphuric acid, and at 100°, five-sixths is given off. F. Ephraim and P. Wagner found that the vap. press., $p$ mm., of the salt is:

| | 50° | 60·5° | 72° | 80° | 80·5° | 86° |
|---|---|---|---|---|---|---|
| $p$ . . | 40 | 80 | 162 | 244 | 260 | 326 mm. |

H. C. Jones and E. Mackay found that the f.p. of soln. with 92·740, 27·822, and 5·564 grms. of $(NH_4)Cr(SO_4)_2.12H_2O$ per litre are, respectively, 0·768°, —0·266°. and —0·064°. P. A. Favre and C. A. Valson gave for the heat of soln. of a mol of the sulphate —9·628 Cals. at 8° to 10°; and —9·889 Cals. at 19° to 21°. They also found for the heat of precipitation of a fresh violet soln. of a mol of ammonium chrome-alum, 14·636 Cals., and after the lapse of 14 days, 13·9 Cals. The corresponding value for a green soln. is 7·641 Cals. C. Soret gave for the index of refraction, $\mu$, between 7° and 14°, for light of different wave-lengths, $\lambda$,

| $\lambda$ . | $G$-line | $F$-line | $B$-line | $E$-line | $D$-line | $C$-line | $B$-line | $A$-line |
|---|---|---|---|---|---|---|---|---|
| $\mu$ . | 1·49594 | 1·49040 | 1·48794 | 1·48744 | 1·48418 | 1·48125 | 1·48014 | 1·47911 |

J. H. Gladstone gave $(\mu-1)/D=0·2781$ for the sp. refraction for the A-line; and $(\mu_A-\mu_G)/D=0·0104$ for the sp. dispersion. J. M. Hiebendaal, and H. Sauer studied the absorption spectrum of ammonium chrome-alum.

DropBooks

H. C. Jones and E. Mackay measured the mol. electrical conductivity, $\mu$ mhos, of the violet soln.; and H. H. Hosford and H. C. Jones gave for soln. with a mol of the violet salt in $v$ litres between 0° and 35°, and S. F. Howard and H. C. Jones, between 35° and 65°,

| $v$ | | 8 | 16 | 32 | 128 | 512 | 1024 | 2048 | 4096 |
|---|---|---|---|---|---|---|---|---|---|
| $\mu$ | 0° | 82·4 | 94·6 | 107·1 | 137·6 | 176·0 | 198·8 | — | 259·0 |
| | 12·5° | 113·1 | 181·0 | 149·1 | 194·5 | 253·0 | 289·3 | — | 378·0 |
| | 25° | 145·9 | 169·6 | 193·8 | 255·7 | 341·2 | 395·3 | — | 523·5 |
| | 35° | 169·8 | 197·9 | 228·6 | 302·7 | 410·2 | 483·1 | 577·4 | 671·2 |
| | 65° | 245·0 | 288·8 | 333·5 | 459·1 | 649·0 | 754·8 | 897·3 | 1050·3 |
| $\alpha$ | 35° | 25·3 | 29·5 | 34·1 | 45·1 | 61·1 | 72·0 | 86·0 | 100·0 |
| | 65° | 23·3 | 27·5 | 31·7 | 43·7 | 61·8 | 71·9 | 85·4 | 100·0 |

The values at the higher temp. are of course affected by the presence of $x$ per cent. of the green salt. $\alpha$ refers to the calculated percentage ionization. The corresponding values for green soln. were :

| $v$ | | 8 | 16 | 32 | 128 | 512 | 1024 | 2048 | 4096 |
|---|---|---|---|---|---|---|---|---|---|
| $\mu$ | 0° | 103·6 | 119·7 | 136·4 | 172·3 | 202·6 | 215·6 | 222·0 | 234·4 |
| | 12·5° | 133·2 | 155·4 | 178·2 | 228·4 | 274·4 | 294·2 | 313·5 | 328·4 |
| | 25° | 162·9 | 190·6 | 220·8 | 288·1 | 355·7 | 386·2 | 414·0 | 458·1 |
| | 35° | 194·0 | 229·8 | 268·0 | 355·6 | 446·1 | 492·2 | 537·1 | 589·8 |
| | 65° | 250·7 | 299·6 | 352·2 | 489·8 | 673·8 | 789·6 | 924·3 | 1061·7 |
| $\alpha$ | 35° | 32·9 | 39·0 | 45·4 | 60·3 | 75·6 | 83·4 | 91·1 | 100·0 |
| | 65° | 23·6 | 28·3 | 33·2 | 46·1 | 63·5 | 74·4 | 87·1 | 100·0 |

According to A. Schrötter, ammonium chrome-alum dissolves in cold water forming a bluish-violet soln. Alcohol precipitates the alum from its violet soln. At about 75° or 80°, the bluish-violet aq. soln. assumes a grass-green colour owing to some molecular change, so that the soln. on evaporation does not yield crystals, but dries to a green mass; nor does the green soln. give a precipitate with alcohol, but it either mixes with it, or forms a substratum with the alcohol floating on the surface. If the green soln. is diluted with water, and left to stand for ten days, the violet alum is gradually reproduced. When a soln. of the violet alum is mixed with an excess of sulphuric acid, then treated with alcohol, the green soln. decanted from the precipitated blue salt, and mixed with so much ammonia that it still remains slightly acid, a dark green, highly acid soln. settles to the bottom. When this soln. is allowed to stand for a long time, it decolorizes, and a light green salt is deposited. It has the composition $14(NH_4)_2SO_4.Cr_2(SO_4)_3.3H_2SO_4.33H_2O$. J. Locke found that at 25° a litre of water dissolves 212·1 grms. of $(NH_4)Cr(SO_4)_2.12H_2O$, or 107·8 grms., *i.e.* 9·75 per cent. of $(NH_4)Cr(SO_4)_2$. As in the case of the chromium salts previously discussed, the soln. of the violet salt in water involves a state of equilibrium between the green and the violet forms, and this is dependent on the temp. The time required for equilibrium is represented by the following observations of I. Koppel on the solubilities, $S$ grams of $(NH_4)Cr(SO_4)_2$ per 100 grms. of soln., after the lapse of the stated intervals of time :

| Time | | 2·5 | 20 | 50 | 100 | 200 | 300 | 400 | ∞ hrs. |
|---|---|---|---|---|---|---|---|---|---|
| $S$ | 0° | 3·82 | 3·68 | 3·73 | — | — | — | — | 3·77 |
| | 30° | 10·6 | 11·9 | 13·12 | 16·25 | 15·2 | 15·7 | 16·0 | 16·00 |
| | 40° | 15·5 | 19·3 | 21·6 | 22·8 | 24·5 | — | 24·8 | 24·70 |

He inferred from conductivity and f.p. determinations that at 0° a sat. soln. of the violet alum has 3·8 per cent. of $(NH_4)Cr(SO_4)_2$; and at 40°, after the elapse of 20 days the same soln. is in equilibrium when about 52 per cent. of the solute is in the violet form and 48 per cent. in the green form; while at 55°, equilibrium occurs when 39 per cent. of violet alum and 61 per cent. of green alum are present. Similar data were obtained with conc. soln. The calculations assume that only one variety of the green salt is produced.

Anhydrous or dehydrated ammonium chrome-alum was obtained by M. Traube

by melting chromic oxide or a chromic salt with an excess of ammonium sulphate. It was also prepared by T. Klobb—*vide infra*, the ammonium trisulphatochromiate. The salt appears in hexagonal plates, or as a pale green powder which, according to P. A. Favre and C. A. Valson, had a sp. gr. of 2·472 at 21·9°. M. Traube found that the salt does not melt nor yet decompose at 350°. It reddens when heated. It is insoluble in cold water; and it is not attacked by boiling water, dil. boiling alkali-lye, or acids, or by conc. hydrochloric acid. T. Klobb said that it is isomorphous with the dehydrated potash-alum and soda-alums and with the corresponding aluminium and ferric salts. A. Recoura obtained what he regarded as a pentahydrate, by dehydrating ammonium chrome-alum.

W. Meyeringh obtained **hydroxylamine chromium sulphate,** or **hydroxylamine disulphatochromate,** $(NH_3OH)_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $(NH_3OH)Cr(SO_4)_2.12H_2O$, in cubic crystals, from a soln. of the component salts. H. Sauer studied the absorption spectrum of this salt and of the methylamine. F. Sommer and K. Weise prepared **hydrazine chromium sulphate,** or **hydrazinium disulphatochromiate,** $(N_2H_5)Cr(SO_4)_2.12H_2O$, which furnishes dark violet octahedral crystals, freely soluble in water. G. Canneri prepared **guanidine disulphatochromiate,** $(C_6H_5N_3)_2.H_2SO_4.Cr_2(SO_4)_3.12H_2O$; it is isomorphous with the corresponding sulphatodialuminate.

A. Schrötter prepared **sodium chromium sulphate,** or **sodium disulphatochromiate,** $Na_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $NaCr(SO_4)_2.12H_2O$, by gradually mixing a mol of sodium dichromate with 3 mols of conc. sulphuric acid so as to avoid much heating; adding alcohol, and then allowing the soln. to stand. Definite crystals were not obtained. E. I. Orloff prepared the salt in crystals by the following process:

> Add 100 grms. of xylene, in small portions at a time and with constant stirring, to a sealed flask containing 300 grms. of sulphuric acid of sp. gr. 1·84; when the xylene has dissolved, add 295 grms. more of the acid, and pour the mixture into a large porcelain dish containing a litre of water, and add 375 grms. of finely powdered sodium dichromate in small portions at a time. The reduction takes place in the cold, and it is completed by warming the liquid which then turns green. The soln. is then evaporated to 1339 grms., and the product poured into flat porcelain dishes, covered, and left to crystallize at room temp. The small crystals can be recrystallized from water by slowly evaporating sat. soln.

A. Schrötter found that the salt loses 16 mols. of water at 100°; and it weathers more rapidly in air than the ammonium or potassium salt. F. Ephraim and P. Wagner found the vap. press., $p$ mm., of the hydrate to be:

| | 51° | 63° | 71° | 76° | 80° | 82·5° | 90° |
|---|---|---|---|---|---|---|---|
| $p$ . . | 43 | 83 | 122 | 162 | 241 | 250 | 382 mm. |

T. Klobb obtained mixed crystals of the anhydrous sodium and ammonium chromium sulphates, $(NH_4,Na)SO_4.Cr_2(SO_4)_3$, by melting together chromic sulphate or chrome-alum with ammonium and sodium sulphates. The hexagonal crystals are isomorphous with the anhydrous alums. A. N. Bach found the transition temp. to be between 60° and 70°.

Crystals of potassium chrome-alum, **potassium chromium sulphate,** or **potassium disulphatochromiate,** $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $KCr(SO_4)_2.12H_2O$, were first obtained by A. Mussin-Puschkin; and J. J. Berzelius obtained the violet crystals by the spontaneous evaporation of a soln. of a mixture of the component salts. A. Schrötter, and F. A. Rohrman and N. W. Taylor obtained it by sat. with sulphur dioxide a sat. soln. of potassium dichromate and conc. sulphuric acid prepared in the cold; N. W. Fischer, M. Traube, and H. Löwel used a modification of the process with alcohol as reducing agent; A. Lielegg used oxalic acid as reducing agent, and, added E. A. Werner, if too little water be present, a complex oxalate is formed. G. Städeler obtained chrome-alum as a by-product in the preparation of acetaldehyde. The manufacture of chrome-alum was described by P. Hasenclever, etc.—*vide supra*, the extraction of chromium. J. Hertkorn obtained it by treating a soln. of chromic sulphate in water or sulphuric acid with

potassium sulphite or hydrosulphite—with or without the addition of a little nitrate or nitrite, and then subjecting it to the action of sulphur dioxide under ordinary and an increased press. H. C. Starck described the preparation of a soln. from ferrochromium, where the sulphuric acid soln. of the alloy is treated with potassium dichromate, heated to the b.p. at atm. press., preferably with the addition of sodium carbonate, or at a higher press. The iron compounds are thus precipitated, and the filtered soln. is treated with potassium sulphate for chrome alum. Processes were also described by A. W. Gregory, and O. Nydegger. H. Chaumat prepared the salt by the electrolysis of a soln. of potassium dichromate mixed with sulphuric acid. The liquor is circulated in the cathode compartment, which is separated from the anode by a porous vessel, the cathode preferably consisting of graphite powder packed round a carbon core. Dil. sulphuric acid is circulated in the anode compartment, and to utilize the $SO_3$-ion, which is disengaged at the anode, the latter may take the form of a copper electrode surrounded by copper shavings, whereby copper sulphate is formed in the course of electrolysis. A. Stiassny, H. N. Warren, F. A. Rohrman and N. W. Taylor, and A. Polis discussed the formation of large crystals of the salt. E. S. Hedges and J. E. Myers studied the periodic crystallization of this salt. Analyses were made by N. W. Fischer, and P. de Boissieu. E. J. Maumené found that the analyses indicated between

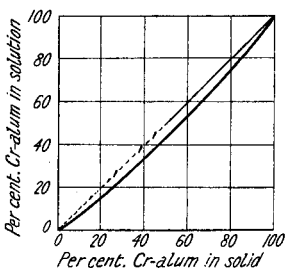



FIG. 81.—Composition of Solution and Solid Mixtures of Potassium Chromium and Potassium Aluminium Alums.

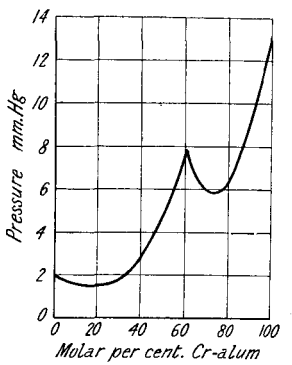



FIG. 82.—Vapour Pressures of Mixtures of Potassium Chromium in Potassium Aluminium Alums.

23·9 and 24·1 mols. of water, and V. A. Jacquelain, 22 mols.—but this number probably refers to the partly effloresced salt. T. Ishikawa studied the reciprocal salt pair $\{K_2,(NH_4)_2\}$—$\{(SO_4),(CrO_4)\}$ at 25°; and A. Fock, and G. Tammann and A. Sworykin, isomorphous mixtures with potash-alum. R. Hollmann's observations on the composition of the solid soln. and mother-liquor for potassium chromium and potassium aluminium alums are summarized in Fig. 81, and his observations on the vap. press. of the solid soln. in Fig. 82. There are two minima, and one maximum in the curve.

The octahedral, cubic crystals are violet to black in colour, and appear ruby-red in thin layers; and J. H. Kastle found that the intensity of the colour is very much reduced at liquid air temp. F. Klocke, C. F. Rammelsberg, C. von Hauer, and J. W. Retgers showed that the crystals are isomorphous with other alums, for they show similar corrosion figures. E. Dittler obtained overgrowth with potassium aluminium sulphate. T. V. Barker found a close connection between parallel overgrowths in chrome-alum, potash-alum, and ammonia-alum and the mol. vols which are respectively 542·2, 541·6, and 552·2. C. von Hauer found that with the introduction of a crystal of iron-alum in a sat. soln. of chrome-alum nearly all the latter separates out; while L. de Boisbaudran found that a sat. soln. of basic ammonium aluminium alum does not affect the octahedral faces of the

crystal, but the cubic faces are slowly attacked. K. Grinakowsky found that different faces of the crystal do not all possess the same solubilities, and that the degree of supersaturation has different values for the different faces of the polyhedron, and is dependent on the temp. At low temp., the edges and angles are the less soluble; and at high temp., the faces; the edges of obtuse angles are more stable than the summits of four-faced angles at low temp., whilst at high temp. the reverse applies. P. N. Pawloff's statement, that the surface layer of a crystalline substance is vectorial in character and influences the direction and general course of the deformation, applies to some extent, especially in the case of twinning deformation. The latter indicates the existence of a temperature-limit for a possible equilibrium of the system crystal-mother liquor, the surface energy being, for a given crystallographic form, a maximum. The direction and course of the deformation of crystals of chrome-alum show that the octahedron is the most stable form, and is followed in order by the rhombic dodecahedron, cube, and trapezohedron. The crystals were studied by E. S. von Fedoroff.

L. Vegard and H. Schjelderup obtained X-radiograms of the alums, and deduced probable arrangements for the metal, sulphur, and oxygen atoms in the space-lattice. They added that the crystal model divides the 24 mols. of water into six groups, which groups are cubically disposed with reference to the four tetrahedrally arranged atoms of sulphur. The model makes no distinction between the water of crystallization and the other constituents of the alum. Any hypothesis which would distinguish the water of crystallization from water of constitution could not be reconciled with the observed relations between the high-frequency reflection spectra. The removal of the water of crystallization is necessarily accompanied by the destruction of that structure which is characteristic of the hydrated salt. The unit hexagonal cells of the anhydrous salt furnished $a=4{\cdot}737$ A., and $c=8{\cdot}030$ A., and each unit cell contains one mol. of $KCr(SO_4)_2$. J. M. Cork found that the unit cubic cell has $a=12{\cdot}20$ A., and that there are four mols. per cell. The eight metal atoms take positions at the corners, centre, centre of faces, and mid-points of the edges of the cell making a rock salt arrangement of the univalent and tervalent metals. C. Schaefer and M. Schubert, L. Vegard and E. Esp, L. Vegard and A. Maurstad, and L. Vegard discussed this subject.

H. Schiff found the sp. gr. to be 1·845; L. Playfair and J. P. Joule, 1·856; H. Kopp, 1·848; J. Dewar, 1·834 at −188°, and 1·82 at 17°; O. Pettersson, 1·842 at 20·8°; J. H. Gladstone, 1·817; while W. Spring gave

| | 0° | 10° | 20° | 30° | 40° | 50° | 60° |
|---|---|---|---|---|---|---|---|
| Sp. gr. | 1·8308 | 1·8282 | 1·8278 | 1·8274 | 1·8269 | 1·8259 | 1·8202 |

According to E. Moles and M. Crespi, the sp. gr. and mol. vol., at 25°/4°, of $KCr(SO_4)_2$ are 2·548 and 111 respectively; of $KCr(SO_4)_2.H_2O$, respectively 2·482 and 120; of $K[Cr(H_2O)_6](SO_4)_2$, respectively 2·17 and 180; and of $K[Cr(H_2O)_6](SO_4)_2.6H_2O$, 1·834 and 272. B. Franz found the sp. gr. of soln. with the following number of grams of $KCr(SO_4)_2.12H_2O$ per 100 grms. of soln., to be at 17·5°,

| Salt | 5 | 10 | 20 | 30 | 40 | 50 | 60 | 70 per cent. |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 1·0174 | 1·0342 | 1·0746 | 1·1274 | 1·1896 | 1·2894 | 1·4566 | 1·6362 |

while G. T. Gerlach gave for violet soln. with 2·84, 5·68, and 8·52 per cent. of the anhydrous salt, respectively 1·0275, 1·055, and 1·0835 at 15°/15°; and for the green soln.:

| $KCr(SO_4)_2$ | 5·68 | 11·36 | 17·03 | 22·71 | 28·39 | 34·07 | 39·74 | 45·42 | 51·10 |
|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 1·050 | 1·103 | 1·161 | 1·225 | 1·295 | 1·371 | 1·453 | 1·451 | 1·635 |

so that the sp. gr. of the violet soln. is greater than is the case with the green soln. M. A. Rakuzin and co-workers found that a sat. soln. of the green alum has 114·19

parts of salt per 100 parts of water at 20°, and the sp. gr. of the sat. soln. is 1·6683. For a concentration $C$ per cent.,

| $C$ . | 5 | 10 | 20 | 40 | 60 | 80 | 100 | 114·19 per cent. |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 1·0378 | 1·0641 | 1·1076 | 1·1623 | 1·2531 | 1·3524 | 1·4404 | 1·6683 |

The sp. gr. of the soln. does not increase proportionally with concentration, and soln. of the same conc. made with different samples of alum have different sp. gr. This is attributed to differences in the relative proportions of the green and violet salts in the different soln. K. Grinakowsky found a transition temp. at 78°; and C. Montemartini and L. Losana, at 77°. P. A. Favre and C. A. Valson, and G. Beck studied the vol. changes which occur when the alum dissolves. J. Beckenkamp found the elastic modulus of the crystals perpendicular to the cubic surface to be 1608 kgrms. per sq. mm.; perpendicular to the dodecahedral surface, 1771 kgrms. per sq. mm.; and perpendicular to the octahedral surface, 1832 kgrms. per sq. mm. A. Ferrero observed that for a 13·75 per cent. soln., at 20·5°, the viscosity is 0·01261 G.G.S. units for the violet soln., and 0·1185 for the green soln. prepared at 80°; similarly for a 20·5 per cent. soln. at 20·5°, 0·01417 for the violet soln. and 0·01294 for the green soln. prepared at 80°. The difference between the green and violet soln. decreases with increasing dilution. R. F. d'Arcy made observations on this subject. F. Rüdorff found that in dil. soln., the potassium sulphate diffuses more rapidly than the chromium sulphate; and D. M. Torrance and N. Knight, G. D. van Cleeff, and M. E. Dougal observed that in the dialysis of the green soln., more sulphuric acid passes through the membrane than is the case with the violet soln. C. Montemartini and L. Losana studied the viscosity of the soln. P. W. Bridgman gave for the compressibility of chrome-alum at 30°, $-\delta v/v_0=64{\cdot}86\times10^{-7}p-112{\cdot}5\times10^{-12}p^2$.

W. Spring gave for the thermal expansion the linear coeff. $0{\cdot}0_4246$ between 0° and 60°. H. Kopp found the sp. ht. to be 0·324. A. Eucken and G. Kuhn found the sp. ht. at −190° to be 0·00242, and the value at 0°, 0·00426. According to C. Pape, the crystals are stable in air; but uninjured crystals effloresce at 29°. N. W. Fischer added that when the salt is impure it will effloresce on the surface when exposed to air, and, if chromic sulphate be in excess, it will assume a green colour, and a violet colour if the potassium sulphate predominates. G. D. van Cleeff, and J. Juttke observed that the salt loses 12 to 13 mols. of water when confined over sulphuric acid, in vacuo; and H. Löwel added that a similar amount is lost over quicklime, or conc. sulphuric acid, at 25° to 30°, and no more is lost by the granular mass at 80° to 90°; at 100° or over, it loses more water and becomes green. J. Juttke observed that all the water can be expelled at 100° without the alum becoming insoluble or decomposing; and G. D. van Cleeff observed a loss of 21 mols. of water at 110°. W. Müller-Erzbach found that at 0·49 mm. press. and 27·8°, half the water of crystallization is given off, and the residue when kept 7 days at 30° loses very little more water. For the dissociation press., $p$ mm. in the reaction: $KCr(SO_4)_2.12H_2O \rightleftharpoons KCr(SO_4)_2.6H_2O+6H_2O$, H. Lescœur and D. Mathurin observed $p=3{\cdot}7$ at 10°; 6·0 at 15°; 9·1 at 20°; 12·3 at 25°; 16·7 at 30°; and 23·8 at 35°; while F. Ephraim and P. Wagner gave

| | 31° | 40° | 50° | 55° | 60° | 70° | 73° | 77·5° | 79° |
|---|---|---|---|---|---|---|---|---|---|
| $p$ . | 15 | 31 | 63 | 86 | 119 | 202 | 224 | 250 | 260 |

R. Hollmann gave $p=13{\cdot}2$ mm. at 17° to 19°; and he also obtained values for solid soln. of the chromium and aluminium alums. H. Lescœur and D. Mathurin found that over conc. sulphuric acid the alum loses half its water of crystallization and passes into a lilac-coloured powder which does not lose its colour at 75°. At 20°, the dissociation press., $p$ mm. of the moist alum, $KCr(SO_4)_2:nH_2O$, is 15·25 mm. for $n=13{\cdot}05$, and 15·0 for $n=12{\cdot}3$; for $n=12{\cdot}1$, $p=9{\cdot}8$, and the violet powder produced when $n=11{\cdot}8$, has $p=9{\cdot}1$. This value

of $p$ remains approximately constant up to $n=6{\cdot}01$. When $n=5{\cdot}72$, a lilac powder is formed with $p=3{\cdot}2$, and for $n=5{\cdot}4$, $p=3{\cdot}2$. When $n=3{\cdot}92$, $p$ is less than $1{\cdot}5$; and when $n=2{\cdot}35$, $p$ is less than $1{\cdot}0$. The $n=6$-hydrate was found by A. Recoura to lose no water between 80° and 90°, but at 110° it gives off 4 mols. and becomes green. A. Beutel found that the velocity with which water is expelled is accelerated by exposing the crystals to visible and ultra-violet light. Observations on the dissociation of the alums were also made by E. J. Maumené, and P. de Boissieu. When the salt is heated to 200°, N. W. Fischer, and C. Hertwig found that 22 mols. of water are given off, and the remainder between 300° and 400°. E. Moles and M. Crespi found that the salt $K[Cr(H_2O)_6](SO_4)_2.6H_2O$ loses about 5·9 mols. of water at 18°, and at 60°; while $K[Cr(H_2O)_6](SO_4)_2$ loses 5·30 mols. of water at 140°; and $KCr(SO_4)_2.H_2O$ loses 0·9 mol. at 350°. According to H. Löwel, when the salt is gradually heated between 300° and 350° it furnishes the anhydrous soluble salt; but over 350°, without losing much weight, it forms the yellowish-green insoluble salt. F. Krauss and co-workers' observations on the effect of heat on potash-chrome-alum can be represented by Fig. 83. The anhydrous salt begins to lose sulphur trioxide at 612°.

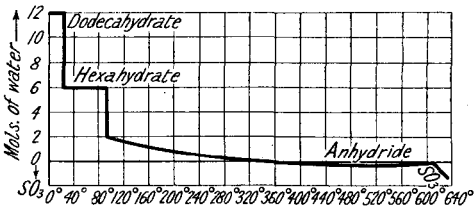



FIG. 83.—The Action of Heat on Potassium Chrome-alum.

The salt melts in its water of crystallization at 80° to 90°. W. A. Tilden, and J. Locke gave 89° for the m.p. H. C. Jones and E. Mackay found for the f.p. of soln. of 117·44, 29·36, and 5·872 grms. of $KCr(SO_4)_2.12H_2O$ in a litre of water, the respective values —0·888°, —0·267°, and —0·065°.

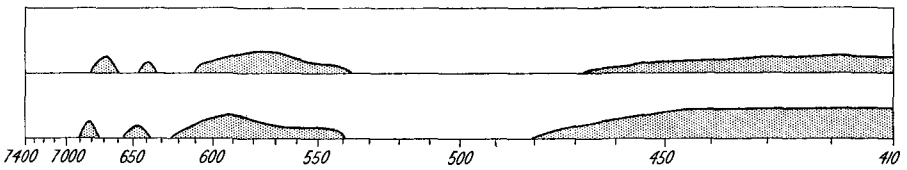
J. Thomsen found the heat of soln. for a mol of $KCr(SO_4)_2.12H_2O$ to be —9·564 Cals. at 8° to 11°; and P. A. Favre and C. A. Valson, —9·651 Cals. at 8° to 11°; and —9·499 Cals. at 19° to 21°. Conc. soln. were found to give almost the same numbers, but the partially dehydrated salt gave 3·825 Cals. H. Löwel, and W. R. Whitney found that barium chloride precipitates all the sulphate from the violet soln. in the cold; and P. A. Favre and C. A. Valson observed that for a mol of $KCr(SO_4)_2$, the heat of precipitation is 14·767 Cals. The heat required for precipitation of the first half of the $SO_4$ is 7·514 Cals., and for the second half, 7·388 Cals.; similarly, for successive quarters, the heats of precipitation are respectively 3·680, 3·702, 3·665, and 3·699 Cals. P. A. Favre and C. A. Valson, and W. R. Whitney, found that only half the sulphate is precipitated at once from the green, modified soln. The total heat of precipitation was found by P. A. Favre and C. A. Valson to be 8·251 Cals. per mol of $KCr(SO_4)_2$, and for the first and second halves 8·142 Cals and 0·204 Cals. respectively; while for the first, second, and third quarters, the values were 4·104 Cals., 4·102 Cals., and 0·146 Cal. respectively. The heat of precipitation for $\frac{1}{2}K_2SO_4$ is 3·3 Cals.; for $\frac{1}{2}Cr_2(SO_4)_3$, 4·9 Cals.; and for $\frac{1}{2}H_2SO_4$, 5·053 Cals. This shows that only half the contained sulphate is precipitable at once by barium chloride from a freshly prepared soln. of the salt.

C. Soret observed that the index of refraction, $\mu$, at 0° to 17°, for light of different wave-lengths, $\lambda$, is:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\lambda$ . | $G$-line | $F$-line | $b$-line | $E$-line | $D$-line | $C$-line | $B$-line | $A$-line |
| $\mu$ . | 1·49309 | 1·48753 | 1·48513 | 1·48459 | 1·48137 | 1·47805 | 1·47738 | 1·47642 |

C. Soret and co-workers found that refractive indices of the green soln. to be less than those of violet soln. J. H. Gladstone gave for the sp. refraction for the $A$-line, $(\mu-1)/D=0{\cdot}2616$; and for the sp. dispersion $(\mu_A-\mu_G)/D=0{\cdot}0098$. J. Formanek

observed that the absorption spectrum of the violet soln., Fig. 84, has a weak band at 671·8, and a stronger one between 610 and 540 with a maximum at 578; at 470, the absorption of short waves begins; J. M. Hiebendaal observed a weak band at 658, and a stronger one between 590 and 535; A. Étard found bands between 678 and 670, and between 654 and 633. O. Knoblauch observed a band between 610 and 558; and W. Böhlendorff, strips at 672, and 640, and a band between 609 and 568. Observations were also made by W. N. Hartley, H. Sauer, G. D. Liveing and J. Dewar, and K. Vierordt. H. W. Vogel found with a violet soln., a strong line at 665, a feebler one at 656, and a broad band with a maximum at 589, and an absorption in the violet begins at 489. The solid salt does not show the first line, and the band is more towards the red. J. Formanek found that the green soln. has a strip at 681, and a second one at 640 which is connected with a band extending as far as 540 with a maximum at 591. The absorption in the violet begins at 480, Fig. 85. J. M. Hiebandaal found with thick layers of soln.




FIGS. 84 and 85.—Absorption Spectra of Solutions of Potassium Chrome-Alum.

a band between 660 and 523, and an absorption beginning at 469; with thinner layers of soln., there are bands between 673 and 667, and between 632 and 544; while with still thinner layers, there is a band between 613 and 535. Observations were also made by W. N. Hartley, and W. Böhlendorff. H. W. Vogel found a small strip at 686, and a band between 656 and 530, while absorption begins at 486. The solid salt, and the alcoholic soln. have different spectra. H. C. Jones and W. W. Strong, K. Grinakowsky, and A. Byk and H. Jaffe studied the violet and ultra-violet spectra of the soln.; H. Sauer, the absorption spectrum. S. Higuchi, the ultra-red spectrum; and H. du Bois and G. J. Elias, the influence of magnetization and temp. on the spectra of the solid salts. H. M. Vernon estimated the ionization from the colour of aq. soln. M. Bamberger and R. Grengg found that the colour fades as the temp. approaches −190°. C. Doelter observed that radium radiations change the crystals into a pale violet powder.

H. C. Jones and E. Mackay, K. Grinakowsky, F. Schmidt, and F. S. Svenson measured the electrical conductivity, $\mu$ mhos, of soln. of the salt; H. H. Hosford and H. C. Jones obtained the accompanying values between 0° and 35°, and S. F. Howard and H. C. Jones between 35° and 65°, for violet soln. containing a mol of $KCr(SO_4)_2.12H_2O$ in $v$ litres. The computed values for the percentage degree of ionization, $\alpha$, are affected by the formation of $x$ per cent. of the green salt.

| $v$ | | 8 | 16 | 32 | 128 | 512 | 1024 | 2048 | 4096 |
|---|---|---|---|---|---|---|---|---|---|
| $\mu$ | 0° | 75·8 | 87·3 | 99·0 | 127·0 | 161·1 | 186·6 | 212·3 | 245·8 |
| | 12·5° | 105·0 | 121·2 | 138·1 | 179·5 | 232·0 | 271·6 | 314·2 | 364·8 |
| | 25° | 135·3 | 157·3 | 179·6 | 236·7 | 311·5 | 369·6 | 428·8 | 500·1 |
| | 35° | 167·0 | 183·3 | 225·8 | 288·1 | 404·1 | 465·4 | 546·9 | 637·4 |
| | 65° | 242·0 | 276·7 | 339·9 | 467·3 | 658·9 | 785·4 | 928·4 | 1083·0 |
| $\alpha$ | 35° | 26·20 | 28·75 | 35·42 | 46·77 | 63·40 | 73·02 | 85·80 | 100·0 |
| | 65° | 22·35 | 25·55 | 31·39 | 43·15 | 60·84 | 72·52 | 85·73 | 100·0 |

V. Monti found that the conductivity of the green soln. is greater than that of the violet soln. H. C. Jones and E. Mackay found that the change from violet to green corresponds with the change in the conductivity of the soln. H. H. Hosford and H. C. Jones, and S. F. Howard and H. C. Jones, obtained the following

results for green soln. for the temp. indicated in connection with the violet soln.:

| | | 8 | 16 | 32 | 128 | 512 | 1024 | 2048 | 4096 |
|---|---|---|---|---|---|---|---|---|---|
| $v$ | . | | | | | | | | |
| $\mu$ | 0° | 107·4 | 126·8 | 146·5 | 188·9 | 224·2 | 244·4 | — | 290·2 |
| | 12·5° | 138·2 | 163·7 | 190·5 | 249·1 | 301·4 | 330·6 | — | 402·8 |
| | 25° | 168·4 | 199·9 | 233·3 | 308·9 | 381·6 | 425·2 | — | 531·5 |
| | 35° | 194·0 | 219·2 | 270·4 | 358·0 | 474·9 | 487·6 | 535·9 | 584·3 |
| | 65° | 248·1 | 279·3 | 352·6 | 486·0 | 699·3 | 771·9 | 903·3 | 1017·0 |
| $\alpha$ | 35° | 33·20 | 37·51 | 46·27 | 61·27 | 81·28 | 83·45 | 91·72 | 100·0 |
| | 65° | 24·39 | 27·47 | 34·67 | 47·78 | 68·76 | 75·90 | 88·81 | 100·0 |

H. T. S. Britton found that, at 18°, a 0·0050*N*- and 0·0067*N*-soln. of the violet and green salts have respectively an e.m.f. of 0·467 and 0·395 volt against a *N*-calomel electrode; the H˙-ion concentrations are $p_H$=3·19 and 1·94; and the percentage hydrolysis is 2·16 and 28·7. In the electrometric titration with sodium hydroxide, precipitation began with the e.m.f. respectively 0·591 and 0·587 volt, when the H˙-ion conc. was $p_H$=5·30 and 5·27; or when 1·00 and 1·21 eq. of alkali per eq. Cr had been added; and precipitation was complete when 2·75 and 2·71 eq. of alkali had been added. F. L. S. Jones studied the formation of complex anions in soln.—*vide supra*, chromic sulphate. According to N. Demassieux and J. Heyrovsky, the polarization curves obtained in the electrolysis of tervalent chromium soln. show inflexions corresponding with either $Cr^{\cdot\cdot\cdot}\rightarrow Cr^{\cdot\cdot}+\oplus$ or $Cr^{\cdot\cdot\cdot}\rightarrow Cr+3\oplus$. The curves show that the less hydrated chromium ions in the green salts are reduced and discharged at potentials which are more positive than those at which the more hydrated chromium ions in the violet salts become reduced. This is true of the chloride and sulphate soln., although with the latter the abnormally great displacements of the potentials at which reduction occurs indicate that the complexity of the ions varies with dilution in passing from the green to the violet form. The potentials at which reduction occurs in potassium and rubidium chrome alum soln. are coincident, and indicate the progressive dissociation of the anion complexes. No reduction occurs in alkaline chromium hydroxide soln., which is regarded as proof of the colloidal nature of the hydroxide, in contrast with soln. of zincates and plumbites in which reduction has been observed.

C. Montemartini and L. Losana studied the e.m.f. of soln. of the salt. A. Hagenbach made observations on the thermoelectric force of the soln. E. Feytis found the magnetic susceptibility of the powdered salt to be $11·83\times10^{-6}$ mass units; J. G. Königsberger found for the soln., $13\times10^{-6}$ mass units at 22°; and O. Liebknecht and A. P. Wills, $22\times10^{-6}$ mass units at 18°. P. Pascal found the mol. magnetic susceptibility to be $2\times629\times10^{-5}$. L. A. Welo's measurements of the magnetic susceptibility of solid and molten alum are summarized in Fig. 86. The Curie point, $C=\chi(T-\theta)$, for the solid and molten potassium chromic alum are $C_s$=2·02, $C_l$=1·67; $\theta_s=-37°$; and $\theta_l$=17°.

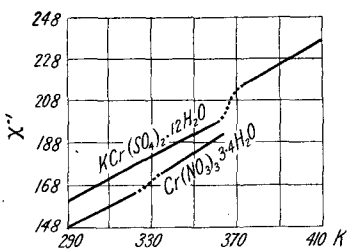



FIG. 86.—The Magnetic Susceptibilities of Hydrated Chromium Salts—Solid and Molten.

N. W. Fischer observed that 100 parts of cold water dissolve 16·7 parts of the chrome alum. J. Locke found that a litre of water dissolves 243·9 grms. of $KCr(SO_4)_2.12H_2O$, or 125·1 grms. of $KCr(SO_4)_2$. The aq. soln. of the violet salt has an acidic reaction, and when the salt has been precipitated many times by alcohol from its aq. soln. H. Baubigny and E. Péchard found that a soln. neutralized by ammonia with methyl-orange as indicator, gave crystals which had an acidic reaction; and the soln. also reacts acidic after standing a little while. F. P. Venable and F. W. Miller also found that the green modified soln. is also acidic. A. and L. Lumière and A. Seyewetz found that a considerable quantity

of alkali-lye can be added to the violet soln. without giving a precipitate; a soln. of 100 grms. of the alum will take up alkali-lye eq. to 8·435 grms. of $H_2SO_4$, at ordinary temp. or at 50°, before it yields a permanent turbidity; at 100°, alkali-lye eq. to 12·8 grms. of $H_2SO_4$ is similarly taken up. F. Ulffers observed that a cold, conc., aq. soln. of the alum takes up nearly a mol of alkali per gram-atom of chromium, and at the same time the soln. becomes green. According to E. J. Mills and R. L. Barr, a turbidity appears in a soln. of chrome-alum when 2 mols of $Na_2CO_3$ per mol of $Cr_2(SO_4)_3$ have been added; and L. Meunier and P. Caste found that chrome alum soln. undergo hydrolysis and the basic chromic salts so formed polymerize under the action of heat and more slowly on keeping. The neutralization of the sulphuric acid formed by the hydrolysis by the sodium carbonate, is accompanied by the liberation of carbon dioxide, and this is expelled from the soln. by increase of temp. or agitation. The precipitation is due to the sodium carbonate acting as a neutralizing agent and also as a coagulating agent on the colloidal soln. of the chromium hydroxide or the polymerized basic chromium salts. For W. J. Chater and J. S. Mudd's observations on the H·-ion conc., *vide supra*, chromium sulphate. The electrometric titration curves of H. T. S. Britton for violet and green soln. of chrome-alum are shown in Fig. 79. N. W. Fischer observed that by the spontaneous evaporation, of the violet soln., the salt may be recovered unchanged; if the soln. be heated between 50° and 75°, it becomes green, and furnishes, on evaporation, a green soluble, amorphous mass or else it yields crystals of potassium sulphate leaving green chromic sulphate in soln.; but H. Löwel added that the chromic sulphate hinders the crystallization of the potassium sulphate. H. Löwel also observed that if the chrome-alum in a sealed tube be melted in its water of crystallization, and cooled to −20°, there remains a viscid liquid, which, when evaporated at 25° to 30°, loses about 18 mols. of water; if allowed to stand 2 or 3 weeks under a bell-jar over water, it takes up 15–20 per cent. of the original quantity. If a soln. of alum be dissolved in twice or thrice its weight of water, the green soln. very slowly deposits crystals of chrome-alum. D. Gernez observed that seeding the green liquid with crystals of alum favours the formation of crystals of chrome-alum. V. A. Jacquelain said that the re-formation of crystals of chrome-alum from the green soln. occurs at 2°; and H. Löwel, at 20° to 30°. H. Löwel also found that if chrome-alum be melted in a sealed tube, or if a soln. of chrome-alum in one or two parts of water be boiled in a flask which is closed while the soln. is boiling, no crystallization occurs even if the vessels be shaken after standing for a year; but the crystallization of the undercooled or supersaturated liquid starts immediately the vessel is opened.

L. de Boisbaudran observed that the violet soln. prepared in the cold gradually becomes greener; while the green soln. prepared by heat, slowly becomes blue. In the former case, the soln. increases in vol. owing to the salt giving up combined water; and in the latter case the soln. decreases in vol. owing to the salt taking up water. K. Grinakowsky said that the absorption spectra, and the electrical conductivities of the soln. indicated that 78° is the transition temp. for the violet to the green soln. The transformation has been discussed by G. D. van Cleeff, M. E. Dougal, W. R. Whitney, A. Recoura, F. P. Venable and F. W. Miller, etc. —*vide supra*, chromic chloride. A. Mitscherlich observed that if the soln.—with or without admixture with potassium sulphate—be heated to 200°, an amorphous precipitate is formed which is supposed to be *chromium-löwigite*, or the *enneahydrate*, $K_2SO_4.Cr_2(SO_4)_3.9H_2O$. F. P. Venable and F. W. Miller said that the same salt is precipitated by adding alcohol to a freshly prepared soln. of the violet salt. According to C. R. C. Tichborne, if a soln. of chrome-alum be heated in sealed tubes for 2 or 3 hrs. at 177°, a basic sulphate is precipitated; and a dil. soln. of chrome-alum is instantly dissociated, or hydrolyzed when dropped into a flasko of biling water, for the contents of the flask become turbid and opaque. The precipitate redissolves on cooling, and even during boiling if the chrome-alum

is gradually added. He concluded that "the green colour of chromic salts is due to the basylous condition"—*vide supra*, H. T. S. Britton's observations. H. Löwel found that barium chloride precipitates all the $SO_4$ from a cold, freshly prepared, violet soln., but only part of the $SO_4$ is precipitated from the green soln., so that when the filtrate is heated, the addition of barium chloride precipitates more $SO_4$. C. Montemartini and L. Losana studied the solubility of the salt in sulphuric acid. According to M. Krüger, alcohol precipitates from the violet soln. the unchanged violet salt—*vide supra*—but the green soln. furnishes a green oily liquid which gradually solidifies, and which contains three-fourths of the $SO_4$-radicle, the remaining quarter remains dissolved in the alcohol; and M. Siewert added that the oily precipitate contains $K_2O : Cr_2O_3 : SO_3 = 6 : 5 : 18$, and the soln. 2 : 3 : 14. G. N. Wyrouboff observed that the same amount of chromic oxalate is precipitated by the addition of alkali oxalate to the freshly prepared violet soln. as to a soln. which has been kept at 30° for some time. H. Löwel observed that zinc and iron react with a soln. of the salt as in the case of chromic chloride (*q.v.*).

As indicated above, H. Löwel found that if chrome-alum be heated gradually between 300° and 350°, it is transformed into green, anhydrous, $K_2SO_4.Cr_2(SO_4)_3$, which is a pseudomorph after the hydrate, and quickly dissolves in boiling water. If chrome-alum be heated a little above 350°, or, according to C. Hertwig, between 300° and 400°, until all the water is expelled, the anhydrous, green, insoluble salt is formed. This salt, said N. W. Fischer, is lilac-coloured when hot, yellowish-green when cold. C. Hertwig, and H. Löwel found that if the salt be heated just below redness it loses 5·8 per cent. of sulphur trioxide, and at a full red-heat, the chromic sulphate forms chromic oxide. The potassium sulphate can be removed by washing with water. The salt is decomposed if boiled for a long time with alkali-lye with the separation of chromic oxide. The salt is not decomposed by cold or boiling water, hydrochloric acid, sulphuric acid, nitric acid, or aq. ammonia. M. Traube heated potassium dichromate with a large excess of conc. sulphuric acid, and at 160° to 180° obtained a mush of a green, insoluble double salt, and a green liquid; at 240°, there is produced a greyish-red substance. These products contain the more potassium sulphate the lower the temp., and the shorter the time of contact with the acid. W. Wernicke obtained some analogous products.

According to N. W. Fischer, and C. Hertwig, a *dihydrate*, $K_2SO_4.Cr_2(SO_4)_3.2H_2O$, is formed when potassium chrome-alum is heated to 200° so long as it continues to lose water. The dark green, porous residue slowly dissolves when boiled for a long time with water, and more rapidly if hydrochloric acid be present. Water and dil. sulphuric or hydrochloric acid do not act on the salt at ordinary temp. in the course of several days. The salt is decomposed by warm, aq. ammonia which separates as dark-green chromic oxide, soluble in hydrochloric acid. P. N. Pavloff studied the action of soln. of chrome-alum on leather. The *enneahydrate*, $K_2SO_4.Cr_2(SO_4)_3.9H_2O$, and the *tetracosihydrate*, ordinary chrome-alum, have been discussed above. F. Fichter and E. Brunner observed that fluorine is a powerful oxidizing agent. They showed that a soln. of chromium alum, acidified with very dil. sulphuric acid, is not altered by the passage of fluorine for several hours, but if the conc. of free acid is as high as 1·5*N*, a regular oxidation to chromic acid sets in, and is easily recognized by the change of colour from violet to orange-yellow. Higher conc. of sulphuric acid up to 7·5*N* have the same effect. The oxidation is certainly indirect, for if the amount of chromic acid is determined by titration, the fresh soln., which evolves ozone, has about 1·5 times the possible oxidizing power. After standing overnight or heating on a water-bath, the excess of oxidizing substances is destroyed, and the soln. has an oxidizing value corresponding exactly to the theoretical amount of chromic acid. The oxidizing substance must be sulphuric tetroxide, for it is effective at 0°, whereas persulphate oxidizes chromic salts only at higher temp. The conc. sulphuric acid is assumed to exert two functions: (i) to furnish sulphur tetroxide as an intermediate com-

pound; and (ii) to prevent the formation of hydrogen dioxide and hence of perchromic acid which would lead to reduction. According to L. Meunier and P. Caste, the amount of sodium carbonate necessary to produce a permanent precipitate in a soln. of chrome-alum varies with the age and method of preparation of the soln. Immediately after the soln. has been prepared, there is a relatively short period during which the amount of sodium carbonate required increases with the time up to a maximum which varies with the dilution and the temp. This period is longer and more marked the more conc. is the soln. and the lower the temp. After this maximum, there is a relatively long second period, which may last several months during which the amount of sodium carbonate required decreases slowly with the time. At high temp., and particularly at 100°, the two periods are of such short duration that the end of their combined action is almost immediate. It is supposed that immediately on its dissolution in water, chromium sulphate undergoes a partial hydrolysis. The chromium hydroxide and chromium sulphate interact to give a less ionized complex more stable towards sodium carbonate. This process predominates at first. This immediate hydrolysis progresses and is slowly accentuated and the ionic conc. is increased until the second process gradually predominates, with the consequent requirement of less sodium carbonate for the precipitation of the chromium hydroxide. F. E. Brown and J. E. Snyder observed that a crystal of chrome-alum blackens when boiled with vanadium oxytrichloride.

T. Klobb obtained hexagonal crystals of **ammonium potassium chromium sulphate,** $(NH_4,K)_2SO_4.Cr_2(SO_4)_3$, as solid soln. isomorphous with the anhydrous alums, by fusing a mixture of potassium chrome-alum with ammonium sulphate. The salt is not attacked by boiling water. By operating in an analogous manner, **ammonium aluminium chromium sulphate,** $(NH_4)_2SO_4.(Cr,Al)_2(SO_4)_3$, and **ammonium ferric chromium sulphate,** $(NH_4)_2SO_4.(Cr,Fe)_2(SO_4)_3$, were obtained as isomorphous mixtures.

J. H. Gladstone, and H. Erdmann prepared **rubidium chromium sulphate,** or **rubidium disulphatochromiate,** $Rb_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $RbCr(SO_4)_2.12H_2O$, from a soln. of the component salts. It furnishes violet octahedra which, according to O. Pettersson, have the sp. gr. 1·968 at 16·8°. J. H. Gladstone gave 1·946 for the sp. gr. J. Locke said that the salt melts at 107° in its water of crystallization. F. Ephraim and P. Wagner found the vap. press., $p$ mm., of the hydrate to be :

| | 40° | 51° | 61·5° | 71° | 79·5° | 84° | 90° |
|---|---|---|---|---|---|---|---|
| $p$ . . | 25 | 42 | 86 | 166 | 250 | 355 | 414 |

C. Soret found the index of refraction, $\mu$, for the wave-length, $\lambda$ at 12° to 17°, to be :

| | $G$-line | $F$-line | $b$-line | $E$-line | $D$-line | $C$-line | $B$-line | $A$-line |
|---|---|---|---|---|---|---|---|---|
| $\lambda$ . | | | | | | | | |
| $\mu$ . | 1·49323 | 1·48775 | 1·48522 | 1·48486 | 1·48151 | 1·47868 | 1·47756 | 1·47660 |

J. H. Gladstone gave for the sp. refraction for the $A$-line $(\mu-1)/D=0·2444$; and for the sp. dispersion $(\mu_A-\mu_G)/D=0·0090$. H. Sauer studied the absorption spectrum. H. Erdmann found that the salt is sparingly soluble in cold water, and that the soln. becomes green when heated. J. Locke gave for the solubility in a litre of water at 25°, 43·4 grms. of the hydrated and 25·7 grms. of the anhydrous salt. N. Demassieux and J. Heyrovsky studied the polarization curves—*vide supra.*

J. H. Gladstone, and C. Soret prepared **cæsium chromium sulphate,** or **cæsium disulphatochromiate,** $Cs_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $CsCr(SO_4)_2.12H_2O$, from a soln. of the component salts. J. H. Gladstone gave 2·043 for the sp. gr. J. Locke found the m.p. to be 116°. F. Ephraim and P. Wagner gave for the vap. press., $p$ mm.,

| | 44° | 71·8° | 80° | 81·5° | 90° | 95° |
|---|---|---|---|---|---|---|
| $p$ . . | 14 | 119 | 224 | 250 | 411 | 512 |

C. Soret observed the index of refraction, $\mu$, for light of wave-length, $\lambda$, at 6° to 12°, to be :

| | $G$-line | $F$-line | $b$-line | $E$-line | $D$-line | $C$-line | $B$-line | $A$-line |
|---|---|---|---|---|---|---|---|---|
| $\lambda$ . | | | | | | | | |
| $\mu$ . | 1·49280 | 1·48723 | 1·48491 | 1·48434 | 1·48100 | 1·47836 | 1·47732 | 1·47627 |

J. H. Gladstone gave for the sp. refraction for the $A$-line $(\mu-1)/D=0{\cdot}2326$ ; and for the sp. dispersion, $(\mu_A-\mu_G)/D=0{\cdot}0086$. H. Sauer studied the absorption spectrum. J. Locke found for the solubility in a litre of water at 25°, 9·4 grms. for the hydrated, and 5·7 grms. for the anhydrous salt. The soln. becomes green above 95°.

E. Carstanjen, J. E. Willm, and O. Pettersson prepared **thallium chromium sulphate,** or **thallium disulphatochromiate,** $Tl_2SO_4.Cr_2(SO_4)_3.24H_2O$, or $TlCr(SO_4)_2.12H_2O$, from a soln. of the component salts. The octahedral crystals appear almost black ; they appear red by transmitted light. J. H. Gladstone gave 2·388 for the sp. gr. ; J. Locke, 92° for the m.p. ; and F. Ephraim and P. Wagner, for the vap. press., $p$ mm.,

| | 33° | 50° | 68° | 78·5° | 87·5° | 94° | 102° |
|---|---|---|---|---|---|---|---|
| $p$ | 8 | 44 | 155 | 250 | 394 | 507 | 672 |

The index of refraction, $\mu$, for light of wave-length $\lambda$ at 9° to 25°, was found by C. Soret to be :

| | $G$-line | $F$-line | $b$-line | $E$-line | $D$-line | $C$-line | $B$-line | $A$-line |
|---|---|---|---|---|---|---|---|---|
| $\lambda$ | 1·53808 | 1·53082 | 1·52787 | 1·52704 | 1·52280 | 1·51923 | 1·51798 | 1·51692 |
| $\mu$ | | | | | | | | |

J. H. Gladstone found the sp. refraction for the $A$-line to be $(\mu-1)/D=0{\cdot}2161$ ; and the sp. dispersion, $(\mu_A-\mu_G)/D=0{\cdot}0092$. H. Sauer studied the absorption spectrum. J. Locke observed that a litre of water at 25° dissolves 163·8 grms. of the hydrated or 104·8 grms. of the anhydrous salt.

A series of salts of the type $3R_2SO_4.Cr_2(SO_4)_3$, or $R_3Cr(SO_4)_3$, or $R_3[Cr(SO_4)_3]$, has been prepared in the dry way, but not by wet processes. The salts may be identical with A. Recoura's chromotrisulphuric acid. T. Klobb found that when chromic oxide, chloride, or sulphate is fused with ammonium sulphate, **ammonium trisulphatochromiate,** $(NH_4)_3Cr(SO_4)_3$, is formed in pale green, acicular crystals, which become rose-coloured when heated. If the fusion is prolonged, anhydrous ammonium chrome-alum is formed. Ammonium trisulphatochromiate is insoluble in cold water, and it is slightly attacked by boiling water, dil. acids, and dil. alkali-lye. It is not changed at 350°, but it decomposes at a red-heat forming chromic oxide. W. Wernicke prepared **lithium trisulphatochromiate,** $Li_3[Cr(SO_4)_3]$, by fusing chromic oxide with lithium hydrosulphate, adding conc. sulphuric acid to the cold mass, and fusing the mixture again. The properties resembled those of the potassium salt. W. Wernicke obtained **sodium trisulphatochromiate,** $Na_3[Cr(SO_4)_3]$, in a similar manner ; and C. Pagel, by melting a mixture of sodium hydrosulphate, and ammonium and chromic sulphates (5 : 2.5 : 1) as in the case of the potassium salt ; and also by heating sodium dichromate and chloride in the presence of an organic reducing agent, and treating the product with sulphuric acid. The salt forms prismatic or acicular crystals, and behaves like the potassium salt. W. Wernicke obtained **potassium trisulphatochromiate,** $K_3[Cr(SO_4)_3]$, by melting potassium pyrosulphate with anhydrous chrome-alum, or chromic sulphate or oxide, and extracting the cold mass with hot water. A. Étard prepared it by melting chromic chloride and potassium hydrosulphate at a red-heat ; and T. Klobb, by melting a mixture of chrome-alum, and ammonium and potassium sulphates (1 : 4 : 4). The green powder was found by W. Wernicke to appear violet-red when hot ; it consists of six-sided rhombic or hexagonal needles. C. Pagel said that the crystals are hexagonal ; and T. Klobb added that they are probably isomorphous with the corresponding ammonium salt. The compound loses $SO_3$ when heated to redness, and, according to W. Wernicke, it is insoluble in water, acids, and dil. alkali-lye, but it is decomposed by boiling with conc. potash-lye.

A. Recoura obtained **potassium chromitetrasulphate,** $K_2[Cr_2(SO_4)_4]$, by evaporating on the water-bath a mol of green chromic sulphate with a mol of potassium sulphate ; and the *tetrahydrate*, $K_2[Cr_2(SO_4)_4].4H_2O$, by dehydrating chrome-alum slowly at 110°. The former compound is dark green, and it is soluble in water.

The soln. gives no immediate precipitation with barium chloride, showing that all the $SO_4$-radicles are masked. The isomeric $(KO)_2Cr_2O_2(SO_3)_4$, or $K_2[Cr(SO_4)_4]$, was obtained from the chromipolysulphuric acid (*q.v.*); and similarly also with **sodium chromitetrasulphate.** A. Recoura obtained **potassium chromipentasulphate,** $K_4[Cr_2(SO_4)_5]$, by evaporating on a water-bath a mol of green chromic sulphate with 2 mols of potassium sulphate; if 3 mols of potassium sulphate are employed, **potassium chromihexasulphate,** $K_6[Cr_2(SO_4)_6]$, is formed. Both these green compounds are soluble in water; and all the $SO_4$-radicles are masked. G. N. Wyrouboff discussed the composition of these salts—*vide supra*, the corresponding acids.

The mixed crystals of potassium sulphate and chromate were discussed in connection with potassium chromate. A. Recoura obtained **potassium chromitrisulphatochromate,** $K_2[Cr_2(SO_4)_3(CrO_4)]$, by evaporating on a water-bath a soln. of a mol of the green sulphate with a mol of potassium chromate. The dark brown, amorphous product forms a green or brown soln. with water; the aq. soln. readily decomposes into chromic sulphate and potassium chromate. A. Recoura also prepared **potassium chromitrisulphatodichromate,** $K_4[Cr_2(SO_4)_3(CrO_4)_2]$, by using a mol of green chromic sulphate and 2 mols of potassium chromate; with three mols of potassium chromate, **potassium chromitrisulphatotrichromate,** $K_6[Cr_2(SO_4)_3(CrO_4)_3]$, is formed. The properties of these salts are similar. According to A. Étard, a soln. of a mol of potassium chromate and 2 mols of magnesium sulphate furnishes monoclinic prisms of **potassium magnesium disulphatochromate,** $K_2CrO_4.2MgSO_4.9H_2O$, which lose 5 mols. of water at 100°, and all the water at 250°. C. von Hauer said that a third of the $SO_4$-radicles in $K_2SO_4.MgSO_4.6H_2O$ can be replaced by the $CrO_4$-radicle without change of form. A. Duffour showed that A. Étard's salt is an arbitrary stage in a series of isomorphous mixtures of $nK_2Cr(SO_4)_2.6H_2O.(1-n)K_2Mg(CrO_4)_2.6H_2O$.

S. M. Jörgensen [2] prepared **chromic hexamminosulphate,** $[Cr(NH_3)_6]_2(SO_4)_3.5H_2O$, by triturating the hexamminobromide with freshly precipitated silver oxide and water; the filtrate was treated with dil. chromic sulphate, and the salt precipitated by alcohol. The yellow needles lose 4 mols. of water over sulphuric acid; and at 100°, the water is expelled in a few hrs. The salt is freely soluble in hot water. It forms a complex chloroplatinate. S. M. Jörgensen, and O. T. Christensen obtained **chromic aquopentamminosulphate,** $[Cr(NH_3)_5(H_2O)]_2(SO_4)_3.3H_2O$, and as in the case of the preceding salt, the prismatic crystals are freely soluble in water; they lose 4 mols. of water between 98° and 100°. The salt forms a complex chloroplatinate. A. Werner and J. L. Klein obtained **chromic tetraquodiamminosulphate,** $[Cr(NH_3)_2(H_2O)_4]_2(SO_4)_3$, by dissolving the bromide in a little dil. hydrobromic acid, adding 8 vols. of absolute alcohol, then adding dil. sulphuric acid, and washing the crystals with alcohol and ether. The reddish-violet plates are very hygroscopic. P. Pfeiffer prepared **chromic tetraquodipyridinosulphate,** $[CrPy_2(H_2O)_4]_2(SO_4)_3.3H_2O$, and also the **hydrosulphate,** $[CrPy_2(H_2O)_4]HSO_4.2H_2O$. For the hexaquo-salts, see the chlorosulphates, and the alums $M[Cr(H_4O_2)_6](SO_4)_2$.

H. J. S. King prepared **chromic hydroxypentamminosulphate,** $[Cr(NH_3)_5(OH)]SO_4$, by the action of a soln. of chloropentamminochloride on ammonium sulphate in conc. aq. ammonia, and precipitation by the addition of alcohol. He gave for the conductivity, $\mu$ mhos, of a mol of the salt in $v$ litres:

| $v$ | | 32 | 64 | 128 | 256 | 512 | 1024 | 2048 |
|---|---|---|---|---|---|---|---|---|
| $\mu$ | 0° | 59·4 | 69·5 | 82·0 | 94·1 | 108·3 | 118·9 | 132·3 |
| | 25° | 117·6 | 132·9 | 158·3 | 181·2 | 208·2 | 234·0 | 254·2 |

A. Werner and J. L. Klein, and A. Werner and J. V. Dubsky obtained **chromic hydroxytriaquodiamminosulphate,** $[Cr(NH_3)_2(H_2O)_3(OH)]SO_4.H_2O$, by the action of sulphuric acid on chromic dihydroxydiaquodiamminochlorobromide. The pale red needles were insoluble in water, and soluble in dil. acetic and propionic acids. The acetic acid soln. with potassium thiocyanate forms dihydroxydiaquodiamminothiocyanate. P. Pfeiffer and M. Tapuach, and P. Pfeiffer and W. Osann

prepared **chromic hydroxytriaquodipyridinosulphate,** $[CrPy_2(H_2O)_3(OH)]SO_4$. O. T. Christensen obtained **chromic nitritopentamminosulphate,** $[Cr(NH_3)_5(NO_2)]SO_4.H_2O$, by the action of silver sulphate on the chloride of the series. The yellow crystals lose water with decomposition at 100°; they are freely soluble in water; and are decomposed by dil. sulphuric acid. S. M. Jörgensen obtained **chromic chloropentamminosulphate,** $[Cr(NH_3)_5Cl]SO_4.2H_2O$, by treating an aq. soln. of the chloride with silver carbonate, and adding dil. sulphuric acid and afterwards alcohol to the filtrate. The carmine-red prisms are freely soluble in water. All the water is expelled in the presence of conc. sulphuric acid, or at 100°, a **hydrosulphate,** $[Cr(NH_3)_5Cl]_4(SO_4)(HSO_4)_6$, was also prepared. A. Benrath found that the chloropentamminosulphate, $[Cr(NH_3)_5Cl]SO_4$, is stable in the presence of 0 to 70 per cent. sulphuric acid, but with more conc. acid, $4[Cr(NH_3)_5Cl]SO_4.3H_2SO_4$ is formed. P. T. Cleve, P. Pfeiffer and S. Basci, P. Pfeiffer and M. Tilgner, and S. M. Jörgensen obtained **chromic chloroaquotetramminosulphate,** $[Cr(NH_3)_4(H_2O)Cl]SO_4$, by the action of cold conc. sulphuric acid on the chloride of the series. The rose-red or dark violet rhombic plates are sparingly soluble in cold water, and freely soluble in warm water. The salt is decomposed by boiling in acidic soln. Y. Shibata measured the absorption spectrum. A. Werner and A. Miolati gave 171·5, 195·1, 226·4, and 262·6 mhos for the conductivity of soln. with a mol of the salt respectively in 250, 500, 1000, and 2000 litres of water at 25°. The pale violet precipitate is hygroscopic. For A. Recoura's, R. F. Weinland and R. Krebs', and R. F. Weinland and T. Schumann's observations on **chromic chloropentaquosulphate,** $[Cr(H_2O)_5Cl]SO_4$, *vide infra*. P. T. Cleve also prepared **chromic bromoaquotetramminosulphate,** $[Cr(NH_3)_4(H_2O)Br]SO_4$, by treating an aq. soln. of the bromide of the series with sodium sulphate and sulphuric acid, and then adding alcohol. The rose-red, crystalline powder is freely soluble in water: and when the aq. soln. is boiled the salt is decomposed with the deposition of hydrated chromic oxide, and the evolution of ammonia. E. H. Riesenfeld and F. Seemann treated a soln. of chlorodiaquotriamminodichloride with conc. sulphuric acid, and obtained pale violet, hygroscopic crystals of **chromic chlorodiaquotriamminosulphate,** $[Cr(NH_3)_3(H_2O)Cl]SO_4$. S. Guralsky, and A. Werner prepared violet **chromic bromodiaquotriamminosulphate,** $[Cr(NH_3)_3(H_2O)_2Br]SO_4$, by the action of sulphuric acid on the chloride of the series followed by alcoholic precipitation; and A. Werner and R. Huber, N. Bjerrum and G. H. Hansen prepared **chromic bromopentaquosulphate,** $[Cr(H_2O)_5Br]SO_4.H_2O$, or $CrBrSO_4.6H_2O$.

P. Pfeiffer and M. Tapuach prepared **chromic dihydroxydiaquodipyridinosulphate,** $[CrPy_2(H_2O)_2(OH)_2]_2SO_4.12$ or $14H_2O$; and P. Pfeiffer and P. Koch, **chromic cis-dichlorobisethylenediaminohydrosulphate,** $[Cr\ en_2Cl_2](HSO_4)$. E. Rosenbohm obtained **chromic dichlorotetramminosulphate,** $[Cr(NH_3)_4Cl_2]_2SO_4$, with the magnetic susceptibility $20{\cdot}68\times10^{-6}$ mass units. A. Werner obtained **chromic dichloraquotriamminosulphate,** $[Cr(NH_3)_3(H_2O)Cl_2]_2SO_4$, by treating the chloride of the series with sulphuric acid. The blue needles form a blue soln. with water; and the salt is reprecipitated by the addition of sulphuric acid. A. Werner, and S. Guralsky prepared dark green crystals of **chromic dibromoaquotriamminosulphate,** $[Cr(NH_3)_3(H_2O)Br_2]_2SO_4$, by the action of sulphuric acid on the bromide of the series. For A. Werner and R. Huber's observations on **chromic dibromotetraquosulphate,** *vide infra*. P. Pfeiffer and P. Koch prepared **chromic cis-dithiocyanatobisethylenediaminohydrosulphate,** $[Cr\ en_2(SCy)_2]HSO_4.1\frac{1}{2}H_2O$; and P. Pfeiffer, the **trans-salt.**

S. M. Jörgensen prepared both the rhodo- and the erythro-salts of **chromic hydroxydecamminosulphate,** $[Cr_2(OH)(NH_3)_{10}]_2(SO_4)_5.2H_2O$, by adding sulphuric acid to an aq. soln. of the thiocyanate of the series. The carmine-red, quadratic or rectangular plates are sparingly soluble in cold water. S. M. Jörgensen prepared carmine-red prismatic crystals of **chromic trihydroxyaquohexamminosulphate,** $[Cr_2(OH)_3(H_2O)(NH_3)_6]_2SO_4.3H_2O$, as well as the **hydrosulphate,** $[Cr_2(OH)(H_2O)(NH_3)_6]HSO_4.\frac{1}{2}H_2O$. P. T. Cleve prepared **chromic decahydroxy-**

**tetramminosulphate,** $Cr_4(OH)_{10}(SO_4)(NH_3)_4.19H_2O$, by the action of ammonia on ammonium chrome-alum. P. Pfeiffer and W. Vorster prepared **chromic hexahydroxysexiesethylenediaminosulphate,** $[Cr_4(OH)_6en_6](SO_4)_3.10H_2O$. M. Z. Jovitschitsch treated a chromium salt with a little aq. ammonia, and about a gram of the light grey hydroxide treated with just enough sulphuric acid to dissolve it, diluted to about 25 c.c., and mixed with the same vol. of ammonia. A grey precipitate is formed which redissolves in an hour or two. When the soln. is treated with alcohol, the red oil which is formed, when freed from ammonium sulphate, solidifies to a red mass of **chromic dioxyhexamminodisulphate,**

$$\begin{matrix}(NH_3)_2{=}Cr.O.NH_3.Cr{=}SO_4\\ (NH_3)_2{=}Cr.O.NH_3.Cr{=}SO_4\end{matrix}\quad 10H_2O$$

When dried over sulphuric acid, it loses $4H_2O$, but when left in contact with water, it gradually suffers hydrolysis and becomes paler, the acid radicles being partly replaced by hydroxyl groups. It is stable in absolute alcohol, but absorbs carbon dioxide when exposed to the air. D. Strömholm prepared **platimic dihydroxysulphatoctamminochromatodichromate,** $[Pt_2(NH_3)_8(OH)_2SO_4]Cr_2O_7(CrO_4)$, as well as **platinic hydroxysulphatotetramminodichromate,** $[Pt(NH_3)_4(OH)(SO_4)]_2Cr_2O_7$, previously obtained by P. T. Cleve.

H. Schiff prepared the monohydrate of **green chromic chlorosulphate,** $CrClSO_4.H_2O$, by evaporating at about 50° a soln. of basic chromic sulphate in cold hydrochloric acid. A. Recoura, and A. Werner and R. Huber obtained the *hexahydrate* by boiling for a quarter of an hour 60 grms. of violet chromic sulphate with 50 c.c. of fuming hydrochloric acid, and allowing the mixture to stand for some days. R. F. Weinland and R. Krebs obtained the *octohydrate* by evaporating at 10° over conc. sulphuric acid a mixture of a conc. aq. soln. of the green chloride with an eq. quantity of sulphuric acid; and R. F. Weinland and T. Schumann, and N. Bjerrum also obtained it from one of the chromic chlorides and sulphuric acid. H. Schiff described his monohydrate as a green, hygroscopic, amorphous mass; A. Werner and R. Huber described his hexahydrate as a bluish-green mass of tabular crystals; and R. F. Weinland and co-workers found the octohydrate forms pale green masses of tabular crystals. A. Recoura, and R. F. Weinland and co-workers said that a *pentahydrate* is formed by heating the higher hydrate at 85°, or exposing it in vacuo over sulphuric acid. A soln. of the salt gives no immediate precipitation with silver nitrate, but a precipitate with barium chloride is formed at once showing that the chloride radicle is masked, but not so with the sulphate radicle. The lowering of the f.p. is rather greater than would correspond with that for the non-oxidized molecule; and the mol. conductivity 76·5 for $v=125$ at 1° corresponds with the dissociation of the salt into two ions. The conductivity gradually increases when the soln. is allowed to stand showing that the salt is gradually resolved into three ions as it is transformed into the violet salt. The formula for **chromic chloropentaquosulphate,** $[Cr(H_2O)_5Cl]SO_4nH_2O$, fits the facts very well; and this, changing to the violet salt, forms $[Cr(H_2O)_6](SO_4)Cl.nH_2O$. N. Bjerrum discussed the case where the sulphate radicle is not immediately precipitable. L. A. Welo gave $19{\cdot}86\times10^{-6}$ for the magnetic susceptibility of $[Cr(H_2O)_6]ClSO_4.2H_2O$, and $19{\cdot}62\times10^{-6}$ for $[Cr(H_2O)_5Cl]SO_4.3H_2O$.

R. F. Weinland and R. Krebs obtained the *octohydrate* of **violet chromic chlorosulphate,** $CrClSO_4.8H_2O$, by mixing 26·6 grms. of the greyish-blue $CrCl_3.6H_2O$ dissolved in 28 grms. of water, with 10 grms. of conc. sulphuric acid mixed with 18 grms. of water, all well cooled. Violet acicular crystals of the salt separate in a few days as the mixture is evaporated in a desiccator; if 11 grms. of water and 10 grms. of conc. sulphuric acid are used tabular crystals are formed. If the octohydrate is kept over sulphuric acid in vacuo it forms the *hexahydrate*. An aq. soln. of the salt evaporated over sulphuric acid yields violet chromic sulphate. An acidified soln., at 0°, gives an immediate precipitation of silver chloride when

treated with silver nitrate, but barium sulphate is not at once precipitated by barium chloride. The mol. conductivity is 116 for $v=125$ at 1°, showing that the salt is not all ionized into three ions. The lowering of the f.p. also gives values rather larger than those required for the non-ionized molecule. The facts are considered to fit the formula for **chromic hexaquochlorosulphate,** $[Cr(H_2O)_6](SO_4)Cl.nH_2O$. A. del Campo and co-workers obtained the violet salt by the action of hydrogen chloride on a cold, conc. soln. of the violet chromic sulphate. E. Moles and M. Crespi gave 1·799 for the sp. gr. of $[Cr(H_2O)_6]Cl(SO_4).H_2O$, at 25°/4°, and 171 for the mol. vol. According to A. Werner and R. Huber, by mixing conc. soln. of violet chromic sulphate, and green chromic chloride, and adding conc. sulphuric acid while the mixture is cooled with iced water, green crystals of the bimolecular, green chlorosulphate, $(CrClSO_4.6H_2O)_2$, thought by A. Werner and R. Huber, and N. Bjerrum to be **chromic dichlorotetraquochromihexaquodisulphate,** $[Cr(H_2O)_6](SO_4)_2[Cr(H_2O)_4Cl_2].2H_2O$. The aq. soln. does not give an immediate precipitation with silver nitrate, but, it does give one with barium chloride. A 1 : 10-soln. of the salt in dil. hydrochloric acid, when sat. with hydrogen chloride, precipitates half the chromium as blue chromic chloride. N. Bjerrum and G. H. Hansen likewise prepared **chromic dichlorotetraqualuminohexaquodisulphate,** $[Cr(H_2O)_4Cl_2][Al(H_2O)_6(SO_4)_2.2H_2O$; and **chromic dichlorotetraquovanadihexaquodisulphate,** $[Cr(H_2O)_4Cl_2][V(H_2O)_6](SO_4)_2.2H_2O$, by the electrolytic *reduction of vanadyl sulphate in the presence of chromic chloride*. A. *Werner and* R. Huber, and N. Bjerrum and G. H. Hansen obtained **chromic dibromotetraquochromihexaquodisulphate,** $[Cr(H_2O)_6](SO_4)_2[Cr(H_2O)_4Br_2].2H_2O$, by the action of hydrogen bromide as in the analogous case of the preceding salt. The dark green plates are soluble in water; and are precipitated from the aq. soln. by sulphuric acid. N. Bjerrum and G. H. Hansen likewise prepared **chromic dibromotetraquoaluminohexaquodisulphate,** $[Cr(H_2O)_4Br_2][Al(H_2O)_6](SO_4)_2.2H_2O$, as well as the corresponding **chromic dibromotetraquoferrihexaquodisulphate,** $[Cr(H_2O)_4Br_2][Fe(H_2O)_6](SO_4)_2.2H_2O$; and dark green crystals of **chromic dibromotetraquovanadihexaquodisulphate,** $[Cr(H_2O)_4Br_2][V(H_2O)_6](SO_4)_2.2H_2O$, by the electrolysis of vanadyl sulphate in the presence of chromic bromide. The corresponding titanium and manganese salts could not be prepared.

S. M. Jörgensen prepared yellow octahedral crystals of **chromic hexamminoiodosulphate,** $[Cr(NH_3)_6](SO_4)I$, by adding ammonium iodide and sulphate to an ammoniacal soln. of the chloride of the series.

N. Larsson prepared **ammonium chromic chloropentaquodichlorosulphate,** $[CrCl(H_2O)_5]Cl_2.(NH_4)_2SO_4.H_2O$, by adding ammonium sulphate to a well-cooled soln. of chromic chloropentaquodichloride; **ammonium chromic chloropentaquodisulphate,** $[CrCl(H_2O)_5]SO_4.(NH_4)_2SO_4$, by adding alcohol to a cold soln. after boiling a mixture of soln. of chromic chloropentaquodichloride and ammonium sulphate; if the soln. contains sulphuric acid, **ammonium chromic chloropentaquosulphatohydrosulphate,** $[CrCl(H_2O)_5]SO_4(NH_4)HSO_4$, is formed; likewise with **hydroxylamine chromic chloropentaquochlorosulphate,** $[CrCl(H_2O)_5]Cl(SO_4).(NH_4O)_2SO_4.2H_2O$; and **hydroxylamine chromic chloropentaquosulphatohydrosulphate,** $[CrCl(H_2O)_5]SO_4.(NH_4O)HSO_4$. Complexes were also prepared with sulphates of *organic* bases—methylammonium, dimethylammonium, tetramethylammonium, ethylammonium, pyridinium, and strychnine.

R. F. Weinland and T. Schumann observed that a soln. of green hydrated chromic chloride and ammonium sulphate in equimolar proportions deposits crystals of **ammonium chromic trichlorodisulphate,** $CrCl_3.2(NH_4)_2SO_4.6H_2O$, or **ammonium chromic trichlorotetraquodisulphate,** $[Cr(H_2O)_4Cl_2]Cl.2(NH_4)_2SO_4.2H_2O$, in the form of large, green, four- or six-sided plates when kept a short time in a desiccator. Only one-third of the chlorine is precipitated immediately by silver nitrate from an acidified soln. of the salt at 0°, whereas all the sulphate is thrown down immediately by barium chloride. N. Larsson prepared this salt as well as **ammonium chromic dichlorotetraquochlorotrisulphate,** $[CrCl_2(H_2O)_4]Cl.3(NH_4)_2SO_4.2H_2O$; and

N. Larsson, and R. F. Weinland and T. Schumann found that **ammonium chromic dichlorohydrosulphatotrisulphate,** $[Cr(H_2O)_4Cl_2]_2SO_4.2(NH_4)_3SO_4(HSO_4)$, separates in green needles from a soln. containing a mol of green hydrated chromic chloride, a mol of ammonium sulphate, and 1 to 3 mols of sulphuric acid. In an acidified soln. of the salt at 0°, silver nitrate does not produce an immediate precipitate, but all the sulphate is at once thrown down by barium chloride. N. Larsson found that chromium dichlorotetraquosulphate forms complex salts with the sulphates of organic bases—methylammonium, tetramethylammonium, ethylammonium, tetraethylammonium, guanidinium, and pyridinium.

J. Meyer and V. Stateczny [3] obtained indications of the existence of **chromyl sulphuryl chloride,** $CrSO_5Cl_2$, formed by the action of sulphur trioxide on a well-cooled soln. of chromyl chloride in carbon tetrachloride, and the mixture heated in a sealed tube at 120°. The brown product fumes in air, it is decomposed by water into sulphur trioxide and chromyl chloride.

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## § 31. Chromium Carbonates

According to A. Moberg,[1] the precipitate produced by adding an alkali carbonate to a soln. of chromous chloride is supposed to be **chromous carbonate,** $CrCO_3$, which is similar in many respects to magnesium, zinc, and ferrous carbonates. When chromous chloride is added to a boiling soln. of potassium carbonate, the reddish-brown precipitate gradually acquires a bluish-green colour provided air be excluded, and the supernatant liquor becomes yellow, and deposits brown-yellow plates, which, when exposed to air, become opaque and green. If these be now placed in water, a yellow soln. and a greenish-blue residue are formed. Again, if a cold soln. of potassium carbonate, freed from air, is employed, a dense yellow powder may be precipitated, or bluish-green flakes—of the same composition—may appear. If the yellow or brownish-red liquid be exposed to air, it turns green, and deposits a green substance; if the liquid be kept in closed vessels, carbon dioxide is evolved and the liquid becomes turbid, and deposits a green, flocculent precipitate which also gives off carbon dioxide, and hydrogen, forming brown, hydrated chromosic oxide. The precipitate obtained with the cold soln. of potassium carbonate, on boiling, gives off carbon dioxide, and then dissolves in acids without effervescence. If potassium hydrocarbonate be employed, a similar product is obtained but containing more carbon dioxide, while the liquid retains more chromous carbonate in soln. H. Moissan obtained the carbonate of a high degree of purity, by adding sodium carbonate to a soln. of chromous chloride while air is excluded. The amorphous, greyish-white carbonate takes up oxygen from air, and when heated it forms chromic oxide and carbon monoxide; it is sparingly soluble in water sat. with carbon dioxide; if allowed to stand in water exposed to air, it becomes red and then changes to bluish hydrated chromic oxide.

G. Baugé prepared a series of double carbonates by the action of a carbonate on moist chromous acetate or tartrate in an atm. of carbon dioxide. He obtained **ammonium chromous carbonate,** $(NH_4)_2CO_3.CrCO_3.H_2O$, by passing a current of carbon dioxide through an ammoniacal soln. of chromous acetate, and washing the precipitate successively with aq. ammonia, alcohol, and ether, and dried in a current of hydrogen charged with ammonia. The same salt was obtained by boiling a soln. of chromous acetate in ammonia with sodium carbonate in a current of hydrogen. The yellow, crystalline powder, when thoroughly dried, is fairly stable in dry air. It is very active chemically. In air, it forms chromic hydroxide, with chlorine it forms chromic chloride; it dissolves in hydrochloric or sulphuric acid forming a blue soln. if air be absent; and hydrogen sulphide converts it into chromic sulphide. G. Baugé obtained impure **lithium chromous carbonate** by adding lithium carbonate to chromous acetate suspended in water. According to G. Baugé, when well washed and moist chromous acetate is mixed with a soln. of sodium carbonate, it first dissolves, and after a time a reddish-brown compound separates; this is washed with water, and afterwards with 98 per cent. alcohol, all the operations being conducted in an atm. of carbon dioxide. When dried in a current of the same gas, the resulting *decahydrate* of **sodium chromous carbonate,** $Na_2CO_3.CrCO_3.10H_2O$, forms microscopic, tabular lozenge-shaped crystals which lose water in vacuo at the ordinary temp. or at 100°. It is very soluble in cold water, but the solubility gradually diminishes, probably in consequence of polymerization. It is a powerful reducing agent, and decomposes water at a little below

100° with liberation of hydrogen. When exposed to dry air, it effloresces, and is afterwards converted into a mixture of sodium carbonate and chromic hydroxide; in moist air, it oxidizes rapidly with development of heat. Chlorine converts it into chromic oxide with liberation of carbon dioxide; hydrogen and hydrogen sulphide have no action on it in the cold, and when heated at 100° in a current of these gases, it yields the monohydrate. Dil. hydrochloric and sulphuric acids dissolve the salt, forming blue soln. The *monohydrate*, $Na_2Cr(CO_3)_2.H_2O$, obtained by the action of a current of an inert gas at 100°, is a yellow powder which becomes brown when heated in vacuo or in a current of hydrogen, but regains its yellow colour on cooling. At 300°, it decomposes into sodium carbonate and chromic oxide. When heated in air, it is converted into sodium chromate; when heated in chlorine it yields chromyl dichloride and chromic oxide; in hydrogen sulphide at about 240°, it yields the red, crystalline chromic sulphide—otherwise it resembles the decahydrate. When chromous acetate is treated with a 20 per cent. soln. of potassium carbonate, **potassium chromous carbonate,** $K_2CO_3.CrCO_3.3H_2O$, is formed in yellow, hexagonal prisms, which at first dissolve in water, but gradually polymerize, whether in soln. or in the solid state, and become less soluble. It is a powerful reducing agent, and decomposes water below 100°; when heated out of contact with air, it becomes brown, but regains its original colour on cooling; at about 280°, it decomposes. When heated in air, it is converted into potassium chromate. If the yellow, complex carbonate is suspended in water and treated with a current of carbon dioxide, or if the chromous acetate is treated with a dil. soln. of potassium carbonate, a less soluble, red double carbonate is formed; it is partially decomposed by water, and decomposes water at 100°. The carbonates of barium, strontium, and calcium have no action on chromous acetate, but magnesium hydrocarbonate converts chromous acetate into reddish-brown **magnesium chromous carbonate** which could not be obtained free from magnesium carbonate, and which decomposes water at 100°.

According to M. Z. Jovitschitsch, chromic hydroxide freed from all traces of alkali and ammonia, absorbs carbon dioxide from the atm. until the saturation limit corresponding with **chromic pentahydroxycarbonate,** $[Cr_2(OH)_5]_2CO_3.8H_2O$, is attained. This substance can be dried at 100° without losing carbon dioxide, but it is decomposed by acids. The graphic formula is supposed to be either

$$CO\begin{matrix}O.Cr_2(OH)_5\\O.Cr_2(OH)_5\end{matrix}.9H_2O, \quad \text{or} \quad O\begin{matrix}Cr_2(OH)_4.O\\Cr_2(OH)_4.O\end{matrix}CO.10H_2O.$$

According to H. Rose, alkali carbonates precipitate from soln. of chromic salts a pale green hydroxide containing more or less carbonate, which on standing becomes blue in daylight, and violet in artificial light. An excess of the precipitant dissolves the precipitate, and the soln. gives no precipitate when boiled; potassium or ammonium hydrocarbonate behaves similarly; but barium carbonate slowly precipitates hydrated chromic oxide completely from cold soln. J. N. von Fuchs made a similar observation with respect to calcium carbonate; and H. Demarçay, with respect to strontium and magnesium carbonates. K. F. W. Meissner, J. Lefort, and T. Parkman obtained basic chromic carbonates by the action of alkali or ammonium carbonate on a soln. of a chromic salt. M. Hebberling added that the freshly-formed precipitate is soluble in soln. of alkali carbonate or borax. The composition of the precipitate depends on the conditions; thus, K. F. W. Meissner gave $10Cr_2O_3.7CO_2.8H_2O$; J. J. Berzelius, $4Cr_2O_3.CO_2.H_2O$; and C. Langlois, $2Cr_2O_3.CO_2.6H_2O$.

T. Parkman dropped a cold, aq. soln. of chrome-alum into a soln. of sodium carbonate with constant stirring until the mixture had only a slight alkaline reaction. The unwashed, moist precipitate corresponded with **chromic oxydicarbonate,** $Cr_2O(CO_3)_2$. If the mixing be done in the reverse way, the precipitate is contaminated with sulphate. J. Lefort treated a violet soln. of a chromic salt with a moderate excess of sodium carbonate and, after washing and drying the product,

obtained **chromic dioxycarbonate,** $Cr_2O_2(CO_3)$. It loses carbon dioxide at 300°. T. Parkman obtained a similar product by adding sodium carbonate to a boiling soln. of chrome alum ; and W. Wallace by adding sodium or ammonium carbonate to a cold dil. soln. of chromic chloride. The washed precipitate was dried at ordinary temp.

O. T. Christensen prepared **chromic nitritopentamminocarbonate,** $[Cr(NH_3)_5(NO_2)]CO_3$, by triturating an excess of silver carbonate with the chloride of the series, and treating the filtrate with alcohol. The yellow, crystalline product could not be obtained pure. It is easily decomposed ; is freely soluble in water ; and the soln. gives the characteristic reactions of the carbonates.

According to N. J. Berlin, chromic carbonate dissolves sparingly in an aq. soln. of potassium carbonate, forming a pale-green soln. which separates on prolonged boiling. If chromic chloride is supersaturated with a conc. soln. of potassium carbonate, very little precipitate is redissolved ; dissolution occurs on mixing more dil. soln. The soln. of hydrated chromic carbonate in a boiling soln. of potassium hydrocarbonate deposits on cooling a complex **potassium chromic carbonate** in pale green crystalline scales, while a soln. of potassium carbonate under similar conditions deposits a pulverulent complex salt on evaporation. A mineral associated with the serpentine and chromite of Dundas, Tasmania, was called **stichtite**—after R. Sticht—by W. F. Petterd,[2] and *chromobrugnatellite*, by L. Hezner. Its composition is that of a **magnesium chromic hydroxycarbonate,** $2MgCO_3.5Mg(OH)_2.2Cr(OH)_3.4H_2O$, like brugnatellite, with chromium in place of iron ; or hydrotalcite with chromium in place of aluminium. The mineral occurs in micaceous scales of a lilac colour. The cleavage is good ; the sp. gr. is 2·16 ; the refractive index, 1·542 ; it is optically uniaxial or feebly biaxial ; the optical character is negative ; and it is feebly pleochroic. Observations on the mineral were made by W. F. Foshag, L. Hezner, and A. Himmelbauer.

The mineral **beresowite,** *beresovite*, or *berezovite* was found by J. Samoiloff [3] in Berezov, Urals. associated with the galena and cerussite. It is a **lead carbonato-chromate,** $6PbO.3CrO_3.CO_2$ ; and it occurs in deep red, birefringent plates of sp. gr. 6·69.


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## § 32. Chromium Nitrates

F. Allison and E. J. Murphy [1] reported the examination of the magneto-optic properties of a soln. of **chromous nitrate,** $Cr(NO_3)_2$. A. A. Hayes observed that a soln. of hydrated chromic oxide in an excess of nitric acid ; or, according to H. Löwel, of a basic nitrate in that acid forms a soln. which is blue by reflected and red by trans-

mitted light. According to J. R. Partington and S. K. Tweedy, a soln. of chromic hydroxide—freshly precipitated from chrome-alum in the cold, and washed with hot water—in cold $4N\text{-}NHO_3$ is green, but in a few days it becomes violet. When kept in a stoppered bottle, it deposits reddish-violet crystals of **chromic nitrate,** $Cr(NO_3)_3.12\frac{1}{2}H_2O$. The *hemipentacosihydrate* melts at 104° to 105°. J. M. Ordway found that the soln. furnishes purple, rhombic prisms of chromic nitrate, $Cr(NO_3)_3.9H_2O$. J. R. Partington and S. K. Tweedy obtained the crystals of the enneahydrate by allowing a soln. of violet chromic chloride in nitric acid to crystallize in a vacuum desiccator. The *enneahydrate* melts at 36·5°, and decomposes at 100°. It is soluble in alcohol. J. R. Partington and S. K. Tweedy gave 66° to 66·5° for the m.p., and there is no sign of a transition at this temp. to a second hydrate. O. M. Halse said that a soln. of hydrated chromic oxide in dil. nitric acid, when evaporated very slowly, deposits violet crystals of the *hemipentadecahydrate*, $2Cr(NO_3)_3.15H_2O$, which melt at 100°, and decompose during dehydration; but J. R. Partington and S. K. Tweedy said that O. M. Halse's salt is really the hemipentacosihydrate. M. Z. Jovitschitsch found that by dissolving chromic oxide in hot, conc. nitric acid, of sp. gr. 1·4, the soln. on crystallization furnish dark brown, monoclinic prisms of the hemipentadecahydrate, $2Cr(NO_3)_3.15H_2O$, with the axial ratios $a:b:c=1{\cdot}4250:1:1{\cdot}1158$, and $\beta=93°\ 10'$. In contact with dry air, the grey coloured *hemienneahydrate*, $2Cr(NO_3).9H_2O$, is formed. The crystals are red by transmitted light; they are not changed by air; and dissolve in water, and alcohol. M. Z. Jovitschitsch found that the evaporation of a nitric acid soln. of chromic oxide yields a dark brown mass which, when dissolved in water and the soln. evaporated, furnishes a dark green, crystalline mass of anhydrous chromic nitrate, $Cr(NO_3)_3$. This is stable in light, and takes up moisture from the air to form the *trihydrate*, $Cr(NO_3)_3.3H_2O$.

I. Traube gave for the sp. gr. of the violet aq. soln. with 3·389, 7·550, 16·536, and 29·082 per cent. of $Cr(NO_3)_3$, respectively 1·02699, 1·06252, 1·14602, and 1·28163 at 15° when the mol. soln. vol. are respectively 47·9, 50·2, 53·7, and 57·7. C. Montemartini and L. Losana studied the viscosity of the soln. H. C. Jones and F. H. Getman measured the sp. gr. and the f.p. of soln. of chromic nitrate. For soln. with 0·0934, 0·3736, 1·1208, and 1·8680, the respective sp. gr. were 1·021, 1·069, 1·203, and 1·334; and the respective f.p. were —0·280°, —2·493°, —11·57°, and —29·50°. J. R. Partington and S. K. Tweedy found the viscosities, $\eta$ dyne per cm. of soln. containing $W$ grms. of $Cr(NO_3)_3$ per 100 grms. of water to be:

| $W$ | | 29·11 | 23·62 | 15·07 | 7·16 | 3·55 |
|---|---|---|---|---|---|---|
| $\eta$ | 18° | 0·01948 | 0·01669 | 0·01373 | 0·01172 | 0·01102 |
| | 25° | 0·01498 | 0·01122 | 0·01050 | 0·00999 | 0·00993 |

C. Montemartini and L. Losana observed a break in the expansion curve of soln. of chromium nitrate. L. R. Ingersoll found for Verdet's constant for the electromagnetic rotatory power for light of wave-length 0·8, 1·0, and 1·25$\mu$, respectively 0·0066, 0·0041, and 0·0025 for soln. of chromic nitrate of sp. gr. 1·087. W. N. Hartley found that two violet soln. of the nitrate showed absorption bands respectively between 5880 and 5570, and 5650 and 5070. The violet soln. becomes green when heated. According to O. Knoblauch, the absorption spectrum of the soln. has a faint band at 6670, and a band between 6160 and 5770, with a small absorption at 513. When the soln. is diluted the band moves to 6180 to 5920. J. M. Hiebendaal observed a band between 6130 and 5320, and absorption from 4540. The addition of ammonium chloride weakens the band, and produces a narrow band at 6370; in alcoholic soln., there is a narrow band at 6370; a band between 6550 and 5350, with a maximum between 6130 and 5500; and absorption from 4600. A. Étard found bands between 6780 and 6700, and between 6540 and 6330. The spectrum was also examined by A. Byk and H. Jaffe. The electrical conductivity of soln. of the nitrate was measured by H. C. Jones and co-workers, and by N. Bjerrum. H. C. Jones and C. A. Jacobson found the mol. conductivity, $\mu$ mhos, of soln. with

a mol of the salt in $v$ litres between 0° and 35°; and A. P. West and H. C. Jones, and E. J. Shaeffer and H. C. Jones, between 35° and 65°:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $v$ | . | 2 | 8 | 16 | 32 | 128 | 512 | 1024 | 2048 |
| $\mu$ | 0° | 92·9 | 125·3 | 138·3 | 147·6 | 158·8 | 201 | 216 | 224 |
| | 10° | 119·5 | 163·2 | 180·9 | 193·9 | 212 | 270 | 292 | 315 |
| | 25° | 164·9 | 228 | 254 | 275 | 305 | 395 | 440 | 467 |
| | 35° | 192·3 | 279 | 312 | 343 | 417 | 504 | 549 | 595 |
| | 65° | 297 | 445 | 504 | 560 | 705 | 869 | 539 | 1032 |
| $\alpha$ | 0° | 41·4 | 55·9 | 61·6 | 65·8 | 70·8 | 89·7 | 96·5 | 100·0 |
| | 35° | 38·0 | 46·6 | 52·2 | 56·8 | 63·7 | 83·6 | 93·4 | 100·0 |

The values for the percentage ionization, $\alpha$, were calculated by H. C. Jones and C. A. Jacobson; and H. M. Vernon calculated the degree of ionization from the colour. N. Bjerrum calculated the percentage hydrolysis, $100\beta$, and the hydrolysis constant $K$ for $Cr(NO_3)_3+H_2O \rightleftharpoons Cr(NO_3)_2OH+HNO_3$, from $K=[H^{\cdot}][Cr(OH)^{\cdot\cdot}]/[Cr^{\cdot\cdot\cdot}]=m\beta^2/(1-\beta)$, from the conductivity, $\mu$ mhos, for soln. with $m$ mols per litre at 19·8°:

| | | | | | | |
|---|---|---|---|---|---|---|
| $m$ | . | 0·02 | 0·01 | 0·005 | 0·0025 | 0·00125 | 0·00625 |
| $\mu$ | . | 265·7 | 299·1 | 316·0 | 345·2 | 374·8 | 406·5 |
| $100\beta$ | . | 5·0 | 7·2 | 9·0 | 14·2 | 18·6 | 26·0 |
| $K$ | . | $0{\cdot}0_452$ | $0{\cdot}0_456$ | $0{\cdot}0_445$ | $0{\cdot}0_449$ | $0{\cdot}0_453$ | $0{\cdot}0_457$ |

so that the average value of $K$ is 0·00054. G. Herrmann said that his attempt to reduce a soln. of chromic nitrate, electrolytically, *wie nicht anders zu erwarten war*, were unsuccessful. L. A. Welo measured the magnetic susceptibility of the solid and molten hydrate, $Cr(NO_3)_3.3{\cdot}4H_2O$, and the results are summarized in Fig. 86. The Curie points, $C=\chi(T-\theta)$, are for the solid and liquid states, $C_s=1{\cdot}90$; $C_l=1{\cdot}50$; $\theta_s=-85°$; and $\theta_l=5°$. P. Philipp found the magnetic susceptibility to be $24{\cdot}09\times10^{-6}$ and $22{\cdot}75\times10^{-6}$ for soln. respectively of sp. gr. 1·3295 and 1·02706.

According to J. M. Ordway, when alkali hydroxide is added to a soln. of chromic nitrate, chromic hydroxide is precipitated. The precipitate appears when more than two-thirds of the acid has been neutralized. This proves that nitric acid can dissolve more chromic hydroxide than corresponds with the normal nitrate. C. Montemartini and L. Losana studied the e.m.f. of the soln. N. Bjerrum and C. Fourholt determined the masked hydroxide, $Cr(H_2O)_6^{\cdot\cdot\cdot}$, by precipitation as cæsium alum. With soln. of chromic nitrate they obtained the results indicated in Table V.

TABLE V.—THE HYDROLYSIS OF SOLUTIONS OF CHROMIC NITRATE.

| *M*-Molar Soln. | Eq. of base present. | Days heated to 75°. | Per cent. latent chromium. | Masked OH-radicles per 100 Cr-atoms. | Masked OH-radicles per Cr-atom in latent basic Cr. |
|---|---|---|---|---|---|
| 0·01 | — | 3 to 4 | 17·6 | 20 | 1·14 |
| 0·05 | — | 7 | 20·1 | 25 | 1·24 |
| 0·01 | — | 5 | 31·4 | 40 | 1·27 |
| 0·05 | 0·5 | 1 to 5 | 47·3 | 57 | 1·21 |
| 0·05 | 1·0 | 2 to 9 | 67·0 | 103 | 1·54 |
| 0·05 | 2·0 | 2 to 3 | 89·0 | 179 | 2·01 |

A. A. Hayes observed that when a soln. of an excess of chromic oxide in nitric acid is evaporated, it does not furnish crystals, but dries up to a gummy, fissured mass which appears dark green by reflected and transmitted light. J. J. Berzelius, and F. Brandenburg made some observations on this subject. H. Löwel assumed that the green soln. obtained by dissolving hydrated chromic oxide in hot nitric acid contains **chromic hydroxydinitrate,** $Cr(OH)(NO_3)_2$. J. M. Ordway obtained what he regarded as the *hexahydrate*, $Cr(OH)(NO_3)_2.6H_2O$, by keeping crystals of the normal nitrate on the water-bath. The dark green residue is soluble in water, forming

a dark brown liquid which contains chromic nitrate and chromate. H. Schiff said that by digesting the warm nitric acid soln. for a long time, the precipitate which is formed contains $Cr_2O_3$ and 1 or $2N_2O_5$. M. Siewert also said that a sat. blue soln. of hydrated chromic oxide in cold nitric acid contains $Cr(OH)(NO_3)_2$; and the green soln. in hot nitric acid, $2Cr_2O_3.3N_2O_5$ or $Cr(OH)_3Cr(NO_3)_3$. J. M. Ordway assumed that the sat. soln. of hydrated chromic oxide in nitric acid contains $8Cr_2O_3.3N_2O_5$, or $3Cr_2O_3.5Cr(NO_3)_3$. By treating chromic acid, or chromates with nitric acid, F. Brandenburg, H. Moser, and K. F. W. Meissner obtained chromic acid associated with nitric acid. J. E. Howard and W. H. Patterson examined the effect of chromic nitrate on the critical soln. temp. of water and isobutyric acid. For V. Ipatieff and B. Mouromtseff's observations on the action of hydrogen under press., *vide supra*, hydrated chromic oxide.

L. Darmstädter [2] heated potassium chromate with two parts of conc. nitric acid and obtained crimson tabular crystals of what he regarded as **potassium nitritodichromate,** $KCr_2O_5(NO_2)$, or

$$\left.\begin{matrix}KO\\NO_2\end{matrix}\right\rangle CrO_2.CrO_3$$

and an excess of nitric acid was said to convert it into **potassium nitritotrichromate,** $KCr_3O_9(NO)_2$. The aq. soln. furnishes potassium dichromate. The salt melts to a dark brown liquid, and at the same time gives off red fumes. G. N. Wyrouboff, and G. C. Schmidt questioned the existence of these salts—*vide supra*.

H. Schiff treated the hydroxydichloride with nitric acid, and on evaporating the soln. obtained **chromic dichloronitrate,** $CrCl_2(NO_3)$, in hygroscopic plates. When heated, it decomposes: $2CrCl_2(NO_3)=2NO_2Cl+Cr_2O_2Cl_2$. The sol. has an acidic reaction; and the salt is soluble in alcohol. If the soln. of the dihydroxychloride in dil. nitric acid be evaporated, **chromic hydroxychloronitrate,** $Cr(OH)(NO_3)Cl$, is formed as a hygroscopic mass. H. Schiff also obtained **chromic sulphatonitrate,** $Cr(NO_3)SO_4$, as a green, hygroscopic mass, by the action of nitric acid on chromic oxydisulphate; and **chromic tetranitratosulphate,** $Cr_2(NO_3)_4SO_4$, as a brown soluble, hygroscopic mass by evaporating a soln. of the basic sulphate in nitric acid at 80°–90°.

S. M. Jörgensen [3] prepared **chromic hexamminotrinitrate,** $[Cr(NH_3)_6](NO_3)_3$, by reducing a soln. of potassium dichromate first by alcohol and hydrochloric acid, and then by the addition of zinc; adding ammonium chloride and ammonia; and allowing the mixture to stand 24 hrs. W. R. Lang and C. M. Carson, and O. T. Christensen treated with nitric acid the product of the action of liquid ammonia on anhydrous chromic chloride. The orange-yellow plates dissolve in water—100 parts of water dissolve 2·5 to 3 parts of the salt. A. Werner and A. Miolati found soln. with a mol of salt in 125, 250, 500, 1000, and 2000 litres at 25° had the respective conductivities $\mu$=341·2, 374·1, 401·1, 425·3, and 444·2 mhos. H. J. S. King also measured the electrical conductivity of soln. of this salt. E. Rosenbohm gave $20·42\times10^{-6}$ mass unit for the magnetic susceptibility. The salt is decomposed by boiling water; and the aq. soln. gives precipitates with hydrobromic, hydriodic, hydrofluosilicic, hydrochloroplatinic, and hydrochloroauric acids, potassium chromate, dichromate, triiodide, and ferricyanide, and sodium dithionate. F. Ephraim and W. Ritter observed that while the hexammine absorbs ammonia gas at low temp., the dissociation curves show no breaks corresponding with the formation of definite ammines. A. Benrath found that in the presence of conc. nitric acid, $[Cr(NH_3)_6](NO_3)_3.HNO_3$ is formed. S. M. Jörgensen also prepared the **hydrotetranitrate,** and a chloroplatinate. P. Pfeiffer prepared **chromic terethylenediaminotrinitrate,** $[Cr\ en_3](NO_3)_3$. O. T. Christensen obtained **chromic aquopentamminotrinitrate,** $[Cr(NH_3)_5(H_2O)](NO_3)_3$, as in the case of the bromide or iodide. The yellowish-red salt is freely soluble in water; it loses water at 100°; and detonates at a higher temp. A. Benrath found that in the presence of nitric acid $[Cr(NH_3)_6](NO_3)_3$ is formed. P. Pfeiffer prepared the **hydrotetra-**

**nitrate.** P. Pfeiffer treated the hydroxyaquotetramminodithionate with conc. nitric acid, and obtained **chromic diaquotetramminohydrotetranitrate,** $[Cr(NH_3)_4(H_2O)_2](NO_3)_4H$, as an orange powder. E. H. Riesenfeld and F. Seemann obtained red crystals of **chromic triaquotriamminodichloronitrate,** $[Cr(NH_3)_3(H_2O)_3]Cl_2(NO_3)$, by treating an aq. soln. of the trichloride with conc. nitric acid, and **chromic nitratodiaquotriamminodinitrate,** $[Cr(NH_3)_3(H_2O)_2(NO_3)](NO_3)_2$, from a soln. of chromium triamminotetroxide in conc. nitric acid. P. Pfeiffer and W. Osann prepared **chromic tetraquodipyridinotrinitrate,** $[CrPy_2(H_2O_4)](NO_3)_3$. M. Kilpatrick studied **chromic hexaureatrinitrate,** $[Cr(NH_2.CO.NH_2)_6](NO_3)_3$. R. Weinland and W. Hübner studied other complexes with organic radicles.

O. T. Christensen obtained **chromic nitritopentamminodinitrate,** $[Cr(NH_3)_5(NO_2)](NO_3)_2$, by the action of ammonium nitrate on a soln. of the chloride. The yellow octahedral crystals are sparingly soluble in water 100 parts of which dissolve 0·67 part of the salt. The salt detonates when heated. F. Ephraim and W. Ritter observed that **chromic aquopentamminotrinitrate,** $[Cr(NH_3)_5(H_2O)](NO_3)_3$, absorbs ammonia gas at a low temp., the decomposition curve shows that possibly a monammine is formed. Ammonia converts the salt into the hydroxypentamminonitrate, $[Cr(NH_3)_5(OH)](NO_3)_3$. F. Ephraim and W. Ritter found that ammonia gas is absorbed by chromic nitritopentamminonitrate, but the decomposition curve shows no breaks. H. J. S. King obtained **chromic hydroxypentamminodinitrate,** $[Cr(NH_3)_5(OH)](NO_3)_2.\frac{1}{2}H_2O$, by the action of the hydroxide on a soln. of ammonium nitrate, and precipitation with alcohol and ether. He gave for the conductivity, $\mu$ mhos, of a mol of the salt in $v$ litres,

| $v$ | . | 32 | 64 | 128 | 256 | 512 | 1024 | 2048 |
|---|---|---|---|---|---|---|---|---|
| $\mu$ | 0° | 106·4 | 115·7 | 124·7 | 132·0 | 138·9 | 141·4 | 152·7 |
| | 25° | 201·5 | 219·4 | 233·6 | 244·3 | 254·2 | 260·8 | 279·9 |

A. Werner and J. von Halban prepared **chromic nitratopentamminodinitrate,** $[Cr(NH_3)_5(NO_3)](NO_3)_2$, by the action of fuming nitric acid on chromic thiocyanatopentamminonitrate, or of nitric acid on aquopentamminohydroxide. The pale flesh-coloured powder is sparingly soluble in water, and the soln. is liable to decompose. A. Benrath found that with nitric acid, $[Cr(NH_3)_5(H_2O)](NO_3)_2$ may be formed. A. Werner and J. von Halban prepared **chromic nitratopentamminodiiodide,** $[Cr(NH_3)_5(NO_3)]I_2$, by shaking up the nitrate with solid potassium iodide and water. E. H. Riesenfeld and F. Seemann prepared **chromic nitratodiaquotriamminodinitrate,** $[Cr(NH_3)_3(H_2O)_2(NO_3)](NO_3)_2$, by the action of conc. nitric acid on the cold on chromic triamminotetroxide. A. Hiendlmayr prepared **chromic fluopentamminodimitrate,** $[Cr(NH_3)_5F](NO_3)_2$, by the action of calcium nitrate on the difluoride. S. M. Jörgensen prepared **chromic chloropentamminodinitrate,** $[Cr(NH_3)_5Cl](NO_3)_2$, by the action of nitric acid on a cold soln. of the chloride of the series. The carmine-red octahedra are soluble in water; at 17·5°, 100 parts of water dissolve 1·4 parts of salt. A. Werner and A. Miolati found that a mol of the salt in 125, 250, 500, 1000, and 2000 litres of water at 25° have the electrical conductivities $\mu$=250·2, 265·9, 279·0, 288, 299·1 mhos respectively. P. T. Cleve, and S. M. Jörgensen prepared **chromic chloroaquotetramminodimitrate,** $[Cr(NH_3)_4(H_2O)Cl](NO_3)_2$, by the action of nitric acid on the chloride of the series. The carmine-red, or purple-red rhombohedral crystals lose no water over sulphuric acid; at 100°, the salt blackens. A. Werner and A. Miolati found that the soln. of a mol of the salt in 125, 250, 500, 1000, and 2000 litres of water at 25° has the electrical conductivity 206·5, 226·4, 244·7, 260·3, and 282·5 mhos respectively. S. M. Jörgensen prepared violet, octahedral crystals of **chromic bromopentamminodinitrate,** $[Cr(NH_3)_5Br](NO_3)_2$, by the action of nitric acid on the chloride of the series; and also reddish-violet crystals of **chromic iodopentamminodinitrate,** $[Cr(NH_3)_5I](NO_3)_2$. A. Werner and J. von Halban prepared **chromic thiocyanatopentamminodinitrate,** $[Cr(NH_3)_5(SCy)](NO_3)_2$.

S. Guralsky prepared **chromic dibromoaquotriamminonitrate,** $[Cr(NH_3)_3$-

$(H_2O)Br_2]NO_3$; P. Pfeiffer and W. Osann, **chromic dihydroxydiaquodipyridinonitrate,** $[CrPy_2(H_2O)_2(OH)_2]NO_3$; P. Pfeiffer and T. G. Lando, and A. Werner **chromic cis-dichlorobisethylenediaminonitrate,** $[Cr\ en_2Cl_2]NO_3$, and P. Pfeiffer and P. Koch, the **trans-salt.** A. Werner obtained greyish-blue needles of **chromic dichlorodiaquotriamminonitrate,** $[Cr(NH_3)_3(H_2O)_2Cl_2]NO_3$, by the action of nitric acid on the chloride of the series. Y. Shibata measured the absorption spectrum. P. Pfeiffer and M. Tapuach prepared **chromic dichlorodiaquodipyridinonitrate,** $[CrPy_2(H_2O)_2Cl_2]NO_3.2H_2O$; P. Pfeiffer and M. Tapuach, **chromic trans-dibromobisethylenediaminonitrate,** $[Cr\ en_2Br_2]NO_3$; **chromic dibromodiaquodipyridinonitrate,** $[CrPy_2(H_2O)_2Br_2]NO_3$; P. Pfeiffer and M. Tilgner, **chromic dithiocyanatotetramminonitrate,** $[Cr(NH_3)_4(SCy)_2]NO_3$; P. Pfeiffer and P. Koch, **chromic cis-dithiocyanatobisethylenediamine,** $[Cr\ en_2(SCy)_2]NO_3$; and P. Pfeiffer, the **trans-salt.** P. Pfeiffer and S. Basci also obtained **chromic oxalatotetramminonitrate,** $[Cr(NH_3)_4(C_2O_4)]NO_3.H_2O$.

S. M. Jörgensen prepared rose-red or pale carmine-red aggregates of needles of **chromic hydroxydecamminopentanitrate,** $[Cr_2(OH)(NH_3)_{10}](NO_3)_5$, by the action of nitric acid on the chloride or bromide of the series. The rhodo-salt so obtained is sparingly soluble in water. S. M. Jörgensen also prepared the erythro-salt in an analogous way. He also obtained **chromic trihydroxyaquohexamminotrinitrate,** $[Cr_2(OH)_3(H_2O)(NH_3)_6](NO_3)_3$, in pale carmine-red needles sparingly soluble in cold water; and the soln. is liable suddenly to precipitate hydrated chromic oxide. The salt decomposes at 100°; and over sulphuric acid, it gives off a mol. of water. R. F. Weinland and E. Gussmann prepared **chromic dihydroxyhexacetatotripyridinonitrate,** $[Cr_3(CH_3COO)_6Py_3(OH)_2]NO_3.5H_2O$; and P. Pfeiffer and W. Vorster, **chromic hexahydroxysexiesethylenediaminohexanitrate,** $[Cr_4(OH)_6en_6](NO_3)_6.6H_2O$.

P. T. Cleve reported the salts **chromic diamminodihydroxydinitrate,** $Cr(OH)_2(NO_3)_2(NH_3)_2.\frac{1}{2}H_2O$; **chromic diamminopentahydroxynitrate,** $Cr_2(OH)_5(NO_3)(NH_3)_2.nH_2O$; and also **ammonium chromic heptamminoctonitrate,** $2Cr(NO_3)_3.2NH_4NO_3.(NH_3)_7.4\frac{1}{2}H_2O$; and **chromic oxalatohemienneamminonitrate,** $Cr(NO_3)(C_2O_4).4\frac{1}{2}NH_3.1\frac{1}{2}H_2O$. M. Z. Jovitschitsch dissolved a gram of hydrated chromic oxide in enough nitric acid, diluted the liquid to 25 c.c., added the same vol. of ammonia, and found that alcohol precipitated a soluble, scarlet mass of **chromic dioxyheptamminotrinitrate,**

$$\begin{matrix}(NH_3)_2{=}Cr.O.NH_3.Cr{=}(NO_3)_2\\ (NH_3)_2{=}Cr.O.NH_3.Cr(NO_3)(NH_3)\end{matrix}\quad 10H_2O$$

R. Weinland and co-workers prepared complex salts of the nitrate with pyridine, *o*-toluidine, guanidine, and aniline.

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## § 33. Chromium Phosphates

A. Moberg [1] added sodium dihydrophosphate to a soln. of chromous salt and obtained a blue amorphous precipitate of **chromous phosphate,** $Cr_3(PO_4)_2.nH_2O$, which rapidly turns green on exposure to air forming, according to H. Moissan, a chromic salt. The precipitate is soluble in acids—*e.g.* in acetic, tartaric, and citric acids. It is insoluble in water, and a little soluble in water containing carbon dioxide. When heated under press. at 100° it remains amorphous. C. U. Shepard found it occurring naturally in green masses; and he called it *phosphorchromite*. A. Colani was unable to prepare **chromous metaphosphate,** $Cr(PO_3)_2$, by the action of fused metaphosphoric acid on chromium or chromous salts, although the method is applicable for the corresponding ferrous salt.

L. N. Vauquelin [2] found that hydrated chromic oxide dissolves in an aq. soln. of phosphoric acid, forming an uncrystallizable, emerald-green liquid. When a soln. of chromic chloride is mixed with potassium phosphate, a green precipitate is obtained, which appears bluish-black after ignition, and yields a greenish-brown powder. If a hot soln. of chrome-alum is treated with an excess of sodium hydrophosphate, hydrated chromic phosphate is precipitated, and when this is heated, it yields brown **chromic orthophosphate,** $CrPO_4$. A. F. Joseph and W. N. Rae observed that the brown anhydrous salt is formed when any of the hydrates is heated to dull redness—*vide infra*. It is very resistant towards chemical agents being insoluble in hydrochloric acid or aqua regia, and only attacked by sulphuric acid when nearly boiling. It is then converted into an earthy-coloured powder, insoluble in water and acids, which appears to be a compound of chromium phosphate and sulphate of indefinite composition. The anhydrous phosphate requires calcining with lime before it can be dissolved by alkali-lye. W. Lapraik found that a soln. of hydrated chromic oxide in phosphoric acid shows an absorption band in

the green. H. T. S. Britton studied the electrometric titration of soln. of chromic sulphate with sodium phosphate. W. J. Sell dialyzed a soln. of chromic phosphate in an ammoniacal soln. of ammonium hydrophosphate, and obtained **colloidal chromic phosphate.** N. R. Dhar and co-workers studied the adsorption of calcium salts by colloidal chromic phosphate. The electrical conductivity of the sol shows that there are no free ions exist in soln., and this is confirmed by the fact that the sol coagulates. J. A. Hedvall and J. Heuberger found that chromic phosphate begins to react with baryta: $2CrPO_4+3BaO=Ba_3(PO_4)_2+Cr_2O_3$ at 342°; with strontia at 464°; and with lime at 517°.

Some green pigments are composed essentially of chromic phosphate. Thus, J. Arnaudon obtained a green pigment by heating to 170°–180° for half an hour a mixture of 128 parts of normal ammonium phosphate and 149 parts of potassium dichromate, and washing the product with hot water. E. Mathieu-Plessy, and G. Köthe, by boiling 10 kgrms. of potassium dichromate in 100 litres of water, and 30 litres of a soln. of monocalcium phosphate, and 2·5 kgrms. of cane sugar; and G. Schnitzer, by melting 36 grms. of crystalline sodium phosphate, 15 grms. of potassium dichromate, and 6 grms. of tartaric acid and washing the product with cold hydrochloric acid, and then with hot water. J. Dingler employed a similar process. A. Carnot boiled a mixture of an alkali chromate, and sodium thiosulphate in the presence of phosphoric acid. W. Muthmann and H. Heramlhof recommended chromic phosphate as a more stable pigment than chromic oxide for high temp. work.

C. F. Rammelsberg showed that when a cold soln. of sodium dihydrophosphate is added drop by drop to an excess of chrome-alum, the precipitate is lavender or violet, amorphous *hexahydrate;* and if this be allowed to remain in contact with the soln. for, say, 48 hrs., it furnishes the dark violet, crystalline hexahydrate. It may be washed by decantation, filtered, and dried in air. If the chrome-alum be not in excess, a violet powder is formed which does not crystallize if allowed to stand for days. H. Schiff added that this compound is formed only in acidic soln. when the chrome-alum is in excess. The triclinic crystals have a sp. gr. of 2·121 at 14°; A. F. Joseph and W. N. Rae gave 2·12 for the sp. gr. of the hexahydrate at 32·5°. All the hydrates at a low red-heat form the black anhydride, which has a sp. gr. 2·94 at 32·5°. The sp. gr. increases during a prolonged ignition owing to the loss of phosphoric oxide. The following data denote respectively the percentage losses and sp. gr.: heated over a bunsen burner for 1 hr., 1·2, and 3·16, and for 3 hrs., 2·4, and 3·29; heated 36 hrs. at 1100°, 4·4, and 3·42; and when heated 36 hrs. in a draught-furnace, 9·8, and 3·66; and for 50 hrs., 11·7, and 3·78. A. Étard stated that the hexahydrate lost 3·5 mols. of water at 100°. H. Schiff said that the hexahydrate forms a green pseudomorph at 100°, and loses 3 mols. of water, and a fourth mol. is not all expelled when kept for 4 days at this temp. H. Schiff said that when the hexahydrate is boiled with acetic anhydride it forms a green salt. C. F. Rammelsberg said that a green phosphate is formed if the chrome-alum soln. be added to an excess of a soln. of sodium dihydrophosphate. C. L. Bloxam acidified the soln. with acetic acid, and boiling the mixture—*vide infra;* and A. Carnot worked with a boiling acid soln. in the presence of sodium acetate—if a chromate soln. is used, it is reduced to the chromic state by the simultaneous addition of sodium thiosulphate. There is some difference of opinion as to the composition of the green hydrate dried at 100°. C. L. Bloxam, and A. Étard regarded it as a *hemipentahydrate;* and C. F. Rammelsberg, and A. Carnot, as a *trihydrate;* while H. Schiff found that the salt obtained by the action of boiling acetic anhydride on the violet hexahydrate is the green *dihydrate.* A. F. Joseph and W. N. Rae who observed no evidence of the existence of the hemipentahydrate or of the trihydrate, but, in agreement with H. Schiff, they observed the formation of the dihydrate, and found that the dehydration does not proceed any further if the boiling be prolonged. If the dry hexahydrate be heated, A. F. Joseph and W. N. Rae observed that the first break occurs when the dihydrate appears. The dihydrate has a sp. gr. of 2·42 at 32·5°; and H. Schiff represented it by the formula $(HO)_2=PO.O.Cr(OH)_2$. If the hexahydrate be left in contact with its mother-

liquor, or with water, it forms a green, amorphous powder of the *tetrahydrate*. This change occurs if the crystals of the hexahydrate be left in contact with water, or with a soln. of sodium phosphate or of chrome-alum. The change is slow at low temp., for at 5° signs of the change appear only after 30 days, whereas at 100°, half an hour's boiling with water suffices for the production of the green, crystalline tetrahydrate. The violet crystals also passed into the green tetrahydrate when kept for 2 years at room temp. in air. The sp. gr. of the tetrahydrate is 2·10 at 32·5°. According to A. Carnot, the green hydrate is sparingly soluble in boiling water, and in soln. of ammonium nitrate, or acetate. C. L. Bloxam found it to be slowly dissolved by boiling conc. hydrochloric acid in sulphuric and hydrochloric acids, but the dihydrate is rather difficult to dissolve in the latter. C. L. Bloxam found that chromic phosphate is oxidized when boiled with nitric acid of sp. gr. 1·4 assisted by a little potassium chlorate. J. Dowling and W. Plunkett stated that the hydrated phosphate is not soluble in acetic acid, but is soluble in mineral acids from which it is precipitated unchanged by ammonia or ammonium sulphide. The hydrated phosphate is readily dissolved by alkali-lye, from which soln. it is deposited by boiling; but, added H. Kämmerer, much of the phosphoric acid remains in soln. A. F. Joseph and W. N. Rae said that chromite soln. are formed by the action of conc. alkali-lye, and that a soln. of sodium carbonate immediately converts the violet hexahydrate into a green basic salt, which retains alkali too tenaciously to be removed by washing. J. A. Hedvall observed that chromic phosphate reacts with barium oxide at 342°, forming barium phosphate and chromic oxide; and it reacts in an analogous manner with strontium oxide at 464°, and with calcium oxide at 517°.

S. M. Jörgensen prepared **chromic hexamminophosphate,** $[Cr(NH_3)_6]PO_4.4H_2O$, by adding sodium dihydrophosphate to a soln. of the hexamminotrinitrate, and then conc. ammonia. The yellow needles are sparingly soluble in water, and freely soluble in dil. acids, from which soln. the salt is precipitated unchanged by ammonia. It loses water slowly when confined in a desiccator over sulphuric acid; and rapidly when heated to 100° in air.

K. Haushofer obtained an acid salt—**chromic trihydrodiphosphate,** $CrH_3(PO_4)_2.8H_2O$—from a soln. of chromic phosphate in phosphoric acid; the triclinic crystals have the colour of chrome-alum, and are stable in air. A. Schwarzenberg obtained pale green hydrated **chromic pyrophosphate,** $Cr_4(P_2O_7)_3$, by adding sodium pyrophosphate to a soln. of chrome-alum; and L. Ouvrard, by melting sodium metaphosphate with chromic oxide. The pale green hydrate darkens at 100°, and loses nearly 3 mols. of water when heated. L. Ouvrard found that the monoclinic prisms obtained by his fusion process have a sp. gr. of 3·2 at 20°. The salt is soluble in soln. of sodium pyrophosphate, in strong mineral acids, in sulphurous acid, and in potash-lye. J. Persoz said that the pyrophosphate is not attacked by ammonium sulphide. A. Rosenheim and T. Triantaphyllides obtained salts of what they regarded as **chromipyrophosphoric acid,** $H(CrP_2O_7)$. Thus, by dropping into a sat. soln. of sodium pyrophosphate soln. a cold, conc. soln. of chromic chloride in conc. hydrochloric acid, grey **sodium chromipyrophosphate** is formed as an *octohydrate*, $Na(CrP_2O_7).8H_2O$, which becomes a pale green *pentahydrate* in a few days. Similarly, there were obtained pale green **potassium chromipyrophosphate,** $K(CrP_2O_7).5H_2O$; and grey, microscopic columns of **ammonium chromipyrophosphate,** $NH_4(CrP_2O_7).6H_2O$.

According to R. Maddrell, if a soln. of hydrated chromic oxide in an excess of dil. phosphoric acid be evaporated to dryness, and the product heated to 360°, **chromic metaphosphate,** $Cr(PO_3)_3$, is formed. K. R. Johnsson obtained it by heating chromic sulphate with metaphosphoric acid so as to drive off all the sulphuric acid; and P. Hautefeuille and J. Margottet, by melting chromic oxide or phosphate with four times its weight of metaphosphoric acid. The salt was prepared by J. Müller by treating 8 grms. of sodium metaphosphate with 300 c.c. of a conc. soln. of chrome-alum, with constant stirring at 70°; this soln. remains clear when

boiled, or diluted with its own vol. of water. If this soln. be stirred for 4 days at ordinary temp. with 9 grms. of sodium metaphosphate, and the dark green solid be washed, and heated to 350°, chromic metaphosphate is produced. P. Hautefeuille and J. Margottet observed that the green, rhombic crystals are isomorphous with the metaphosphates of iron, aluminium, and uranium; K. R. Johnsson found the sp. gr. to be 2·974, and the mol. vol. 195. A. F. Joseph and W. N. Rae found that if heated for some time over a meker burner, it becomes brown, but regains its green colour on cooling; its sp. gr. is then 2·96, whilst the salt prepared by R. Maddrell's process had a sp. gr. of 2·93. The salt is insoluble in water and in mineral acids. P. Glühmann found that a violet crystalline or green amorphous **chromic triphosphate** is produced by the action of sodium triphosphate on a chromic salt—*vide* **8**. 50.

L. J. Cohen could not prepare **ammonium chromium phosphate,** by adding ammonium dihydrophosphate to a strongly acidic soln. of chromic chloride, but by reducing the acidity, a green, gelatinous precipitate with the composition $(NH_4)_2HPO_4.2CrPO_4.3H_2O$ was obtained; but if no hydrochloric acid or only a very small proportion was present **ammonium chromium hydroxyphosphate,** $5NH_4(H_2PO_4).2CrPO_4.4Cr(OH)_2$, was produced. L. J. Cohen found that the precipitate obtained on boiling soln. of chromic salts with sodium phosphate and acetic acid, is not, as C. L. Bloxam supposed, an impure chromic phosphate, but rather **sodium chromium phosphate,** $Na_2HPO_4.2CrPO_4.5H_2O$, which, when repeatedly washed with water, is converted into a basic salt. H. Grandeau obtained pale violet crystals of **potassium chromium phosphate,** $3K_2O.2Cr_2O_3.3P_2O_2$, by fusing a mixture of chromic and potassium phosphates.

K. A. Wallroth prepared **sodium chromium pyrophosphate,** $NaCrP_2O_7$, by cooling a molten mixture of microcosmic salt and chromic oxide; and L. Ouvrard obtained from a soln. of chromic oxide or chromic phosphate in molten sodium metaphosphate; or of chromic phosphate in molten sodium pyrophosphate. The green rhombic prisms have a sp. gr. 3·0 at 20°. S. M. Jörgensen treated a soln. of chromic hexamminonitrate with sodium pyrophosphate and then with ammonia. Yellow, six-sided plates of **sodium chromic hexamminopyrophosphate,** $Na[Cr(NH_3)_6]P_2O_7.11\frac{1}{2}H_2O$, were produced. The salt is insoluble in cold water; and when confined over sulphuric acid for a few months, it loses $10\frac{1}{2}$ mols. of water; at 130°, some ammonia as well as water is given off. J. Persoz treated a soln. of a chromic salt with potassium pyrophosphate, and obtained a soln. which was not precipitated by ammonium sulphide. L. Ouvrard melted potassium metaphosphate with chromic oxide, or potassium dichromate with chromic phosphate and obtained monoclinic prisms of **potassium chromic pyrophosphate,** $KCrP_2O_7$, of sp. gr. 3·5 at 20°.

C. Friedheim and I. Mozkin [3] prepared **ammonium phosphatotetrachromate,** $(NH_4O.CrO_2.O.CrO_2.O)_2 : PO.(ONH_4)$, by evaporating soln. of a mol each of ammonium dichromate and phosphorus pentoxide or from a soln. of equimolar proportions of ammonium dihydrophosphate and chromium trioxide, or by heating a mixture of 2 mols of phosphoric acid, 4 mols of chromium trioxide, 2 mols of ammonia, and a mol of ammonium dihydrophosphate. The salt forms dark red crystal aggregates; when the soln. of the salt is recrystallized from its aq. soln., ammonium dichromate, and phosphoric and chromic acids are formed. They also prepared **potassium phosphatodichromate,** $(KO.CrO_2.O.CrO_2.O)(KO) : PO.OH$, from a mixture of potassium dichromate with an excess of phosphoric acid. M. Blondel obtained it by mixing a highly conc. soln. of phosphoric and chromic acids, containing 8 mols of the latter to one mol of the former, with three-fourths of a mol of potassium carbonate. A salt of the composition $3K_2O.P_2O_5.8CrO_3$, or **potassium phosphatotetrachromate,** $(KO.CrO_2.O.CrO_2.O)_2PO(OK)_2$, is precipitated in the form of small, short prisms. If the soln. contains only two mols of chromic acid, needles of the phosphatodichromate are formed. If the latter soln., however, is mixed with some crystals of the first salt, the precipitate at first consists of phosphatotetrachromate, but, if left in contact with the liquid, it is converted into

the phosphatodichromate. The phosphatotetrachromate is converted into the phosphatodichromate by treatment with water or with a sat. soln. of potassium dichromate. For some complex phosphohalides, *vide supra*, chromyl chloride.


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